LAGRANGIAN MODELS OF THE DISPERSION OF AIRBORNE CHEMICALLY REACTING CONTAMINANTS

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RESEARCH REPORT AND PROPOSITION

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RESEARCH REPORT

Lagrangian Models of the Dispersion of Airborne Chemically Reacting Contaminants

ABSTRACT

The present work attempts to obtain a mathematical model for generation and dispersion of photochemical smog. A simplified kinetic model which is proposed by FRIEDLANDER and SEINFELD (1969), is presented for the photochemical smog reactions. To take into account the effect of atmospheric mixing processes on the chemical reactions, the Lagrangian similarity hypothesis for the diffusion of non-reactive components is extended to reacting species. The concept of a variable volume batch reactor model (VVBR) is applied in the study of the formation of photochemical smog. The critical value, $[h/b u_*]_{cr.}$ where h is the source height, b constant and u_* friction velocity, for the onset of photochemical smog is found.

Calculations based on the simplified kinetic model and the applications of the Lagrangian similarity hypothesis are given for a nonlinear, second order chemical reaction. Finally, determination of the probability density function of the pollutant is given for the non-reacting case.

I. INTRODUCTION

A. Air Pollution and Photochemical Smog

Air pollution refers to the presence of anthropogenic foreign substances (other than O_2, N_2 and noble gases), either reactive or non-reactive in the atmosphere. When the concentration of these foreign substances increases to a certain degree, they interfere with human beings and their environment, and air pollution is said to be created. The term "smog" originated in Great Britain as a popular derivation of "smoke-fog". Smog has been popularly used to describe any air pollution accompanied by a decrease in visibility. Unless smog is controlled, it will inevitably become a serious threat to the health and environment of the living beings on the earth, especially in urban and industrial areas.

In general, we can distinguish two types of smog, viz., chemically reactive and non-chemically reactive. The constituents emitted directly from sources are usually termed primary contaminants. If these primary contaminants are mainly responsible for the observed effects of air pollution and if they are dispersed in the atmosphere without undergoing chemical change, then these primary contaminants are non-chemically reactive pollutants; for example, carbon monoxide and lead particles.

Constituents which are not emitted directly from sources in appreciable quantities but are formed in the atmosphere from chemical reactions among the primary contaminants are called secondary contaminants. If these secondary contaminants are mainly responsible for the observed effects of air pollution, then these secondary contaminants become chemically reactive air pollution. For example, ozone[1], nitrogen dioxide (also a primary contaminant), oxidized organic products such as

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[1] Ozone is also produced naturally.

PAN's (Peroxyacyl Nitrates), formaldehyde, etc., (which may be mainly responsible for eye irritation) from the reactions between automobile exhausts, oxygen, sunslight, etc., constitute the kind of chemically reactive air pollution that is popularly called photochemical smog. In short, photochemical smog is the result of a series of ultraviolet-initiated* reactions involving hydrocarbons or other organic compounds and nitric oxide. Its chief source is automobile exhaust, which is comprised of carbon monoxide, formaldehyde and other partially oxidized hydrocarbons and noxious gases. It has been established that photochemical smog is a chemically reacting type of air pollution (Leighton, 1961; Wayne, 1962; Altshuller and Bufalini, 1965; Stephens, 1966, 1969; Haagen-Smit and Wayne, 1967). In the Los Angeles basin there is good evidence (Middleton and Haagen-Smit, 1960; Haagen-Smit, 1952) that the hydrocarbons and oxides of nitrogen from automobile exhausts are strong contributors to the production of smog during those days when air circulation is low and there is an abundance of sunlight. Several thousand different organic compounds and other oxidants are produced by chemical and photochemical reactions. Some of the components that are emitted or produced cause eye irritation, plant and animal damage, loss of visibility, and odor, and they are possible health hazards to exposed persons.

The formation of photochemical smog over an urban area is controlled by the rate at which reactants (primarily unburned hydrocarbons and nitric oxide) are introduced into the atmosphere, the mixing of the air masses, the temperature and solar radiation. Because of these many factors which influence the existence of the smog problem, a systematic approach toward the control of air pollution is required.

As a first step in the control of air pollution, air control regions have been established incorporating two or more communities that have a common air pollution problem (Sec'y., HEW, 1968). Each region is responsible for the development of local air quality standards. The control of air pollution in each region may be achieved by either

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* 3100-4000 Å wavelength, less than 3100 Å does not penetrate the lower atmosphere.

(i) modification of the state of atmosphere, or

(ii) controlling, distributing (geographically), or removing the source of pollutants

or both to reach the present air quality standards. For example, the California Department of Public Health has established the following standards for carbon monoxide: 30 ppm for an 8-hour exposure; 120 ppm for a 1-hour exposure. Standards for nitrogen oxides have been based on atmospheric coloration and levels likely to cause long-term health impairments. Oxidant levels have been tentatively set as 0.1 ppm for a 1-hour average, not to be exceeded more than one percent of the time. The present study will be to concentrate on (ii). The problem then is to determine the concentration of air pollutants concentration at any time, at any location for a given emission source and meteorology of the control region. Conversely, the question corresponds to given present standard (say for motor vehicle emission standards, see Table I), what can be the maximum input source allowed? To provide a basis for answering such questions, it is necessary to have reliable models for predicting the pollutants concentration at any time, any location in the control region.

In principle, the above question can be answered, at least in part, through solutions of the equation of continuity for each species in a turbulent medium (BIRD, et. al., 1960, p. 557) provided the meteorology is known,

$$\frac{\partial c_i}{\partial t} + \vec{v} \cdot \vec{\nabla} c_i = \vec{\nabla} \cdot D_i \vec{\nabla} c_i + r_i \qquad (1)$$

where we assume the air density is constant, D_i is molecular diffusivity in the air, r_i chemical reaction rate and c_i the concentration of species i, $\vec{v}$ the wind velocity vector. In a turbulent flow c_i will be a fluctuating function of time. It is then convenient to replace c_i by the sum of a time-smoothed value $\bar{c}_i$ and a turbulent concentration fluctuation c_i' :

$$c_i = \bar{c}_i + c_i' \tag{2}$$

Similarly, replace v_i by $\bar{v}_i + v_i'$ and neglect the molecular diffusion. Then, after time averaging, we have

$$\frac{\partial \bar{c}_i}{\partial t} + \left(\frac{\partial}{\partial x} v_x \bar{c}_i + \frac{\partial}{\partial y} v_y \bar{c}_i + \frac{\partial}{\partial z} v_z \bar{c}_i\right) + \left(\frac{\partial}{\partial x}\overline{v_x' c_i'} + \frac{\partial}{\partial y}\overline{v_y' c_i'} + \frac{\partial}{\partial z}\overline{v_z' c_i'}\right) = \bar{r}_i\left(\bar{c}_1 + c_1', \cdots, \bar{c}_n + c_n'\right) \tag{3}$$

The term $\overline{v_i' c_i'}$ describes the turbulent mass transport. One way of solving Eqn. (3) is to replace the turbulent mass vector $\overrightarrow{v' c_i'}$ by a relation analogous to Fick's law of diffusion:

$$\overline{v_j' c_i'} = -K_j \frac{\partial c_i}{\partial x_j} \qquad j = x, y, z \tag{4}$$

where K_j is the turbulent diffusivity or eddy diffusivity in the j-direction. Further assuming $\bar{r}_i(\bar{c}_1 + c_1', \cdots, \bar{c}_n + c_n') = \bar{r}_i(\bar{c}_1, \cdots, \bar{c}_n) + r_i'$ and neglecting the fluctuating term r_i', we thus obtain the equation of continuity for a species i in turbulent atmosphere transport with chemical reaction:

$$\frac{\partial \bar{c}_i}{\partial t} + v_x \frac{\partial \bar{c}_i}{\partial x} + v_y \frac{\partial \bar{c}_i}{\partial y} + v_z \frac{\partial \bar{c}_i}{\partial z} = \frac{\partial}{\partial x}\left(K_x \frac{\partial \bar{c}_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial \bar{c}_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial \bar{c}_i}{\partial z}\right) + \bar{r}_i \tag{5}$$

Equation (3) with appropriate boundary conditions is the fundamental equation of this research in determining the concentration distribution of airborne pollutants. Eqn. (5) is obtained by assuming turbulent mass flux analogous to Fick's law of diffusion. It is nonlinear (because of $\bar{r}_i$), simultaneous, n coupled partial differential equation. In general, the solution of the above equation requires information on the meteorological conditions (wind speed, solar radiation, etc.), the eddy diffusivities K_x, K_y, K_z, and chemical reaction rate $\bar{r}_i$.

The mathematical modeling of an air

quality control region for photochemical smog includes the following steps (SEINFELD, 1969):

1. determination of meteorological factors influencing the dispersion of airborne pollutants,
2. determination of a suitable kinetic mechanism for the atmospheric chemical reaction of airborne pollutants,
3. combination of above two to formulate a model predicting pollutant concentration distribution as a function of time and location.

A major objective of this research is the investigation of step (3). In the present study, step (2) is based on the mechanism proposed by Friedlander and Seinfeld (1969). In future work, a more sophisticated mechanism may be applied. Information on step (1) comes mainly from meteorological studies. The effect of meteorology on air pollution has been reviewed recently by Panofsky (1969) and Neiburger (1969). They can be summarized briefly as follows:

1. The effect on transport of pollutants is mainly due to the wind.
2. The effect on atmospheric dispersion depends on mean wind speed and on the characteristics of atmospheric turbulence.
3. The effect on the "effective" emission height depends critically on the difference between the temperature of the effluent and that of surrounding air.
4. The effect on chemical reaction rate constants are influenced by temperature for thermochemical reaction and sunlight intensity for photochemical reactions (SEINFELD, 1969).

B. Mathematical Model of Photochemical Smog

It has been pointed out in part A that the main effort of this research is to construct a simple model for combining the information of meteorological conditions and chemical kinetic mechanism to formulate a numerical technique for predicting the pollutant concentration distribution. A direct approach to the above problem is to find the solutions of Eqn. (5). In the case of non-chemically reacting pollutants, numerous solutions to (5) have been obtained for different sources using different expressions for the eddy diffusivities K_x, K_y and K_z (PASQUILL, 1962). In fact, the diffusivities are complicated functions of position in the turbulent field. For this reason, the direct solutions of Eqn. (5) have not been very satisfactory (mainly the boundary conditions have been unrealistic and wind field not accounted for) in prediting atmospheric concentrations except in some very idealized cases. This approach is mainly a numerical calculation of simultaneous partial differential equations on a spatial domain representing an urban area subject to the appropriate boundary conditions. However, lack of detailed knowledge of eddy diffusivities, atmospheric turbulence characteristics in the presence of buildings, wind patterns, etc. makes this approach difficult at present. The direct approach toward the solution of Eqn. (5) will, therefore be bypassed by a more simplified model which is computationally feasible yet still (hopefully) retain the essential aspects of the physical situation. The direct approach will be used only as a check to the simplified model. The simplified model in which we are going to apply the prediction of chemically reacting airborne pollutants is called the Lagrangian similarity model. In this model, the Lagrangian similarity hypothesis proposed by Batchelor (1964) for the non-chemically reacting turbulent diffusion is extended to the reacting case (FRIEDLANDER and SEINFELD, 1969). The so-called Lagrangian similarity hypothesis is that the turbulent motion of particles in a steady, self-preserving,

free shear flow possesses similarity in the Lagrangian sense. The hypothesis was proposed for the non-reacting turbulent diffusion, but in the present study, the Lagrangian similarity hypothesis will be extended to chemically reacting airborne pollutants following FRIEDLANDER and SEINFELD (1969). An initial study for a binary chemically reacting puff has been given by Friedlander and Seinfeld (1969). The form of the concentration distribution in the puff either can be found from empirically determined probability function or direct derivation of the process. In the chapter V, the concentration distribution function is derived for the non-reacting case.

In the formulation of the problem, we consider a puff released from a source near the ground. A puff of contaminant is an ensemble of marked fluid particles that were all at a definite position at the time of release. If the spacing between particles is sufficiently large, then the separate fluid particles move independently and the statistical properties of the motion of a single fluid particle may be obtained by observing the cloud. As the cloud expands in the direction downwind and vertical direction, it is convenient for our observation to follow the cloud (Fig. 1). For this reason the Lagrangian description of flow field is adopted. This approach permits a prediction of the average form of variation of the distribution of the concentration at a given time, but

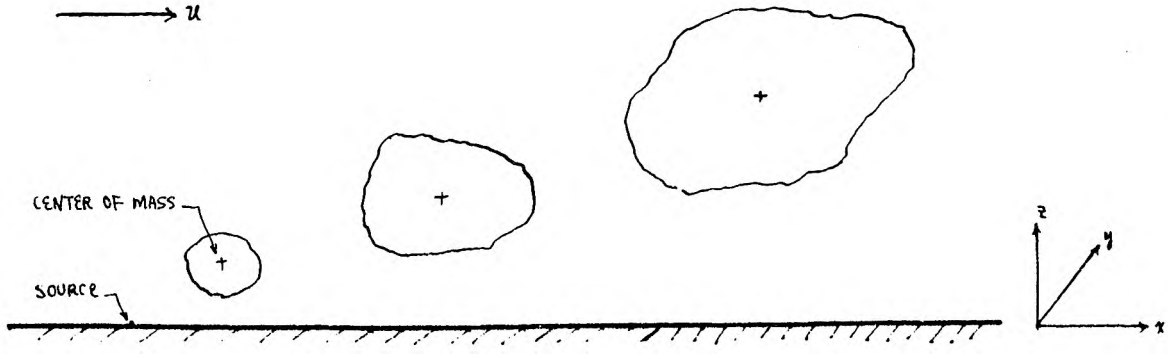


Fig. 1. Expansion of a Contaminant Puff

it is hindered by the difficulty of making any direct measurements of Lagrangian statistics and absence of any simple relations connecting them with the more accessible studies Eulerian statistics of the velocity at fixed point in the flow. We will show later in this report that the Lagrangian similarity hypothesis (Batchelor, 1964) can resolve the above difficulty for practical purposes. The similarity hypothesis does not relate fundamentally the two systems, however.

II. CHEMICAL KINETIC MODEL

Chemical kinetic modeling depends on the understanding of chemical reaction mechanisms for smog formation. The kinetic modeling of photochemical smog includes the following steps:

1. The compilation of published mechanisms for the photochemical smog reactions and integration of the rate equations for a constant volume batch reactor to find the concentration as a function of time for the key constituents.
2. The compilation of published experimental data on the irradiation of mixtures typical of automobile exhausts and comparison of the results from the first step with the experimental observation.
3. The derivation of new kinetic models to incorporate effect or information which might be lacking in currently proposed mechanisms.

Based on this approach, Friedlander and Seinfeld (1969) were able to formulate a kinetic model describing the photochemical smog. The model will be described briefly. It will be referred to as ultrasimplified model.

A. Ultrasimplified Model of Friedlander and Seinfeld

The absorption by NO_2 of the ultraviolet portion of sunlight (3100-4000 Å) results in the following reactions:

$$NO_2 + h\nu \xrightarrow{k_1} NO + O \qquad (6)$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M \qquad (7)$$

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2 \qquad (8)$$

When reactive hydrocarbons are added to the system (atmosphere), many additional reactions take place producing such characteristic products as formaldehyde, acetaldehyde, aerolein, peroxyacyl nitrates (PAN), and alkyl nitrites. It is assumed that the reaction involving hydrocarbon is chain-like reactions:

Initiation step:

$$RH + O \xrightarrow{k_4} R\cdot + \text{PRODUCT} \tag{9}$$

$$RH + O_3 \xrightarrow{k_5} \text{PRODUCTS (INCLUDING } R\cdot) \tag{10}$$

propagation and branching step:

$$NO + R\cdot \xrightarrow{k_6} NO_2 + R\cdot \tag{11}$$

terminating step

$$NO_2 + R\cdot \xrightarrow{k_7} \text{PRODUCTS (INCLUDING PAN'S)} \tag{12}$$

where RH represents reactive hydrocarbon, R· free radicals.

The principal assumptions of the above model are summarized as follows:

1. The major species observed include reactive hydrocarbon, nitric oxide, ozone, nitrogen dioxide, oxygen atom, and R·.
2. O and O_3 and free radicals R· are in pseudo-steady state.
3. The principal initiation step is reaction (9).
4. Reaction (11) embraces all the propagation steps.
5. The principal termination step is reaction (12).
6. k_4' is assumed constant (see below).

Based on the above assumption, we reach the following chemical reaction rate equations:

$$\frac{d[NO_2]}{dt} = [NO_2][RH]\{\alpha[NO] - \lambda[NO_2]\} \tag{13}$$

$$\frac{d[NO]}{dt} = -\alpha[NO_2][NO][RH] \tag{14}$$

$$\frac{d[RH]}{dt} = -[NO_2][RH]\{\theta + \mu/[NO_2]\} \tag{15}$$

where $\alpha = \gamma k_6 k_4'$ (16

$$\lambda = \gamma k_7 k_4' \tag{17}$$

$$\theta = \gamma k_4 \tag{18}$$

$$\mu = \beta k_5 \tag{19}$$

$$k_4' = \frac{k_4}{k_7[NO_2] - (\epsilon - 1) k_6 [NO_2]} \tag{20}$$

ϵ = number of free radicals R· generated as a result of propation and branching in reaction (11).

$$\gamma = k_1/k_2 \tag{21}$$

$$\beta = k_1/k_3 \tag{22}$$

With specific initial concentrations of various constituents Eqns. (16) - (18) can be integrated numerically. The Runge-Kutta method has been used in solving these equations by using IBM 360/75 computer at the California Institute of Technology. The results are also plotted by a Calcomp plotter. Even though there are only three differential equations in this particular model, the computer program can handle a much more general and complicated mechanism.

The parameter values $\alpha = 0.1\ ppm^{-2}min^{-1}$

$$\theta = 1.83 \times 10^{-3}\ ppm^{-1}min^{-1}$$

$$\mu = 2.45 \times 10^{-4}\ min^{-1}$$

$$\lambda = 0.02\ ppm^{-2}min^{-1}$$

were used. These were based on rate coefficients given by Leighton (1961) but were adjusted to simulate the experimental observations. Fig. 2 represents the dynamics for $(NO_2)_0 = 0.2$ ppm

$(NO)_0 = 1.0$ ppm

$(RH)_0 = 2.0$ ppm

Fig. 3 shows the case of

$(NO_2)_0 = 0.2$ ppm

$(NO)_0 = 0.68$ ppm

$(RH)_0 = 1.15$ ppm

The shapes of the curves are in general greement with those found in irradiation chamber experiments (see Fig. 4). As Fig. 4 shows (Tuesday, 1961) nitrogen dioxide forms and nitric oxide disappears as soon as irradiation begins. Acetaldehyde, methyl nitrate and carbon dioxide also form immediately. Compound X* is not formed until all of the nitric oxide present has been oxidized to nitrogen dioxide or methyl nitrate. In continuous radiation experiments ozone is only detectable after nitric oxide has disappeared.

Smog-chamber experiments have been performed at the Battelle Memorial Institute, General Motors Corp., Los Angeles Air Pollution Control District (LAAPCD), National Air Pollution Control Administration, Stanford Research Institute and the U.S. Department of Interior's Bartlesville Petroleum Research Center. Some of the conclusions based on this research are the following:

(1) Control of reactive hydrocarbons (such as olefins and alkylbenzenes) resluts in a reduction of all smog-causing

* Product of the photochemical reaction of nitrogen dioxide and various organic compounds.

reaction products over a considerable range of hydrocarbon to nitrogen oxide level.

(2) An appreciable amount of oxidants are formed even in a very low ratio of nitrogen oxide to paraffinic hydrocarbons or acetylene.

(3) Control of nitrogen oxide does not appear to be nearly as effective as hydrocarbon control in reducing oxidant level.

B. Relation of Eschenroeder Model to the Ultrasimplified Model.

The ultrasimplified model proposed by Friedlander and Seinfeld (1969) is very similar to one proposed later by Eschenroeder (1969). Eschenroeder's model also employs simplified kinetics for the photochemical smog, and at the same time is in conformity with the physical realities of both chamber experiments and atmospheric observations.

In comparing the ultra-simplified model and the "compact chemical reaction scheme" of Eschenroeder (1969), we find that the only differences are (see Fig. 5):

1. The reaction

$$R\cdot + O_2 \longrightarrow R\cdot + O_3$$ is absent in the ultrasimplified model.

2. No steady-state assumption for ozone in Eschenroeder's model.

The reaction rate constant of the above reaction is estimated about 2.3×10^{-5} $ppm^{-1}min^{-1}$, therefore this reaction will explain the difference between these two models. The rate constants in the "compact chemical reaction scheme" (see Table II) are estimated from literature other than those of ultrasimplified model. It does, therefore, validate the ultra-simplified mechanism.

3. The rate constant k'_4 is assumed constant in the ultrasimplified model, while in Eschenroeder's model it is a function of the reaction rate of RH, concentrations of nitrogen dioxide and nitric oxide.

In the following, a comparison is made of the ultrasimplified model A (Friedlander and Seinfeld) and "compact chemical reactions model B (of Eschenroeder).

	A	B
Species observed*	RH, NO, NO_2, O_3, O, R·	RH, NO, NO_2, O_3, R· CHO, O, RCO_x, PAN
Primary reaction (1)	$h\nu + NO_2 \xrightarrow{k_1} NO + O$	$hr + NO_2 \rightarrow NO + O$
Nitric oxide attack by ozone (2)	$NO + O_3 \xrightarrow{k_3} NO_2 + O_2$	$NO + O_3 \rightarrow NO_2 + O_2$
Closing this reversible reaction cycle (3)	$O + O_2 + M \xrightarrow{k_2} O_3 + M$	$O + O_2 + M \rightarrow O_3 + M$
RH is attacked by O (4)	$RH + O \xrightarrow{k_4} R\cdot$ + products	$RH + O \rightarrow^{**}$ (b)RCO_x + (c) R· CHO
RH is attacked by O_3 (5)	$RH + O_3 \xrightarrow{k_5}$ products (including R·)	$RH + O_3 \rightarrow$ (b) RCO_x + (c)R· CHO
Propagation steps (6)	$R\cdot + NO \xrightarrow{k_6} NO_2 + R\cdot$	$RCO_x + NO \rightarrow NO_2 + RCO_{x-1}$
(6a)	———	$O_2 + RCO_x \xrightarrow{k_{6a}} O_3 + RCO_{x-1}$
(7)	$NO_2 + R\cdot \xrightarrow{k_7}$ products (incl. PAN)	$NO_2 + RCO_x \rightarrow$ (a)≠ PAN

	A	B
Pseudo-steady state assumption of O	reactions (1), (3), (4)	reactions (1), (3), (4)
concentratration of free radical (steady-state assumption of free radical)	$(R\cdot) = \frac{k_4[O][RH]}{k_7[NO_2] - (\epsilon-1)k_6[NO]} = k_4'[O][RH]$	$(RCO_x) = \frac{-b\frac{d}{dt}[RH]\cdot[O]\cdot[RH]}{k_6[NO] + k_{6a} + k_7[NO_2]} = k_4'[O]\cdot[RH]$
pseudo steady-state assumption of O_3	Yes	No
is k_4' a constant	Yes	No

* R· in ultrasimplified model is equivalent to RCO_x in compact chemical reaction model.

** Where (b) and (c) represents effective stoichiometry of the product.

≠ Where (a) represents the fraction of the products in the class of PAN's

In summary, these two models are essentially the same in main features. Therefore, in this report the ultrasimplified model will be adopted in the investigation of photochemical smog.

III. LAGRANGIAN SIMILARITY HYPOTHESIS FOR NON-CHEMICALLY REACTING DIFFUSION

A. Theory

The basic theory of the Lagrangian similarity hypothesis for diffusion in turbulent boundary layers was first proposed by Batchelor (1959). Since then, the idea has been used by a number of researchers in various applications (ELLISON, 1959; GIFFORD, 1962; CERMAK, 1963). A brief review of the idea was given by Batchelor himself in 1964.

We shall consider a non-chemically reacting pollutant and one which does not influence the motion of the fluid, i.e., is passive. It will be further assumed that the pollutant (or marked fluid particle) follows the motion of the fluid without displaying any molecular diffusion. Although some controversy still persists concerning the importance of molecular diffusion, it seems unlikely that it is significant in real geophysical situations.

Suppose the strength and geometry of the source is given, so that pollutant is being added to the fluid at a known rate, $Q(x, y, z, t)$ with dimension of mass per unit time per unit volume. Continuous or instantaneous point or line sources may be represented by taking limiting forms for Q in the obvious way (in the instantaneous point source $Q_{ips} = \int_0^\infty\int_{-\infty}^\infty\int_{-\infty}^\infty Q(x, y, z, t)\,dx\,dy\,dz\,dt = Q_0$

continuous point source $Q_{cps} = \int_{-\infty}^\infty\int_{-\infty}^\infty\int_{-\infty}^\infty Q(x, y, z, t)\,dx\,dy\,dz = Q(t)$

continuous line source $Q_{cls} = \int_{-\infty}^\infty\int_{-\infty}^\infty Q(x, y, z, t)\,dx\,dz = Q(y, t)$).

The problem is to find the statistical properties describing the resulting distribution of concentration. The statistical properties means the average of the experiments repeated many times (viz. ensemble mean). For example, in the case of instantaneous point sources, if the experiment is repeated many times, the mean position of the particle at any time t is $\bar{x}(t)$, $\bar{y}(t)=0$, $\bar{z}(t)$ where x axis is the direction downwind and z axis is vertical to the ground.

The concept of similarity may be applied to either Eulerian or Lagrangian systems. In the former case, it is applied to statistical functions relating to the velocity of the fluid at a "given" point in space. In the latter case, it is applied to statistical functions relating to the velocity of a material element of fluid or marked fluid particle. It also permits a prediction of the form of the variation of the dispersion of the concentration at any time; but it is hindered by the difficulty of measuring the statistical properties of the velocity of a marked fluid particle, and its relation to the extensive studied Eulerian statistics. Therefore, the Lagrangian similarity must be introduced as a hypothesis.

Let us consider the region of the fluid near the boundary in which the Reynolds stress (tangential to a flat surface) is constant. Assume the ground is an infinite plane. In the constant stress region, the Eulerian properties depend on z and the shear stress, τ_0, acting on the ground only. We will see later this corresponds to the fact that the structure of the turbulence in the constant stress region is wholly determined by the friction velocity, $u_* (=\sqrt{\tau_0/\rho})$. The mean Eulerian properties of the turbulent motion are independent of position in the xy plane. Hence, these Eulerian properties in the constant stress region are determined by u_* and z. If the mean wind is $\bar{u}(z)$, it follows that

$$\frac{d\bar{u}(z)}{dz} = \frac{u_*}{kz} \tag{23}$$

where k is von Karman's constant, equal 0.4

By using the Prandtl's hypothesis for the turbulent shearing stress (Bird, et al., 1960),

$$\tau = \rho l^2 \left|\frac{d\bar{u}}{dz}\right| \frac{d\bar{u}}{dz} \tag{24}$$

where l is Prandtl's mixing length, ρ the density of the fluid, one can also derive equation (23) using the assumption that turbulent shearing stress in the region near the wall is constant. In the neighborhood of the wall, the mixing length may be assumed proportional to distance from the wall. The assumption is justified by the fact that the turbulent shearing stress at the wall is zero due to the disappearance of the fluctuations. Therefore

$$l = kz \tag{25}$$

and

$$\tau = \rho k^2 z^2 \left(\frac{d\bar{u}}{dz}\right)^2 \tag{26}$$

Prandtl further assumed that the turbulent shearing stress τ is constant in the boundary layer, and is equal to the shearing stress at wall, τ_o. Defining the friction velocity $u_* = \sqrt{\tau_o/\rho}$, Eqn. (26) becomes

$$\frac{d\bar{u}(z)}{dz} = \frac{u_*}{kz} \tag{23}$$

On integration of Eqn. (23) we have

$$\bar{u}(z) = \frac{u_*}{k} \ln \frac{z}{z_o} \tag{27}$$

where z_o is the length characterizing the roughness of the boundary. The whole structure of turbulence will be affected only when z is of the order of z_o.

In the turbulent flow field, a marked fluid particle migrates through a region in which the velocity fluctuation at a given point is statistically steady and depends only on u_* and height z above the ground. If marked fluid particles are released continuously from a fixed source at time t after release, the velocity will vary from one particle to another. The average of some function of velocity over all these particles will depend on t and u_* only. Therefore, Batchelor (1964) proposed the following hypothesis for the ground level sources. "The statistical properties of the velocity of a marked fluid particle at time t after release at the ground level depend only on u_* and t".

In the case of elevated sources, the height of the source, h, above the ground will effect the statistical properties of the velocity of a marked fluid particle at the instant when the particle was released. However, after a certain period of time, the statistical properties of the velocity of a marked fluid particle will lose its dependence on h. The above hypothesis may, therefore, be extended in the following form (Batchelor, 1964):

"The statistical properties of the velocity of a marked fluid particle at time t after release at height h above the ground are the same as those of a particle release at the ground at the instant $-t_1$, provided that $t \gg t_1$, where t_1 is expected to be the order of magnitude of the time scale of the turbulence at height h, i.e., of order h/u_*."

The Lagrangian similarity hypothesis is limited to steady, self-preserving, free shear flow which possess similarity in the Lagrangian sense. The theory proposed by Batchelor (1957) is applicable only to a turbulent shear flow produced by flow along a solid boundary in the region where the shearing stress may be assumed constant and equal to the shearing stress at the wall. In this region (called the constant stress region) the Eulerian

properties are determined by friction velocity and distance from the boundary. In the atmosphere, the thickness of this region is typically between 30 ~ 300 feet above the ground level.

The similarity hypothesis stated above is valid only in adiabatic conditions (i.e., neutral stability). In the case of stable or unstable stratifications (i.e., upward turbulent flux of heat exists), the Lagrangian similarity is extended by including the Monin-Obukhov length, L. This length scale is defined by

$$L = \frac{u_*}{k\, g/T\, (-q/c_p \rho)} \tag{28}$$

where k is von Karman's constant, g the acceleration of gravity, T the average absolute temperature, q the heat flux in the vertical direction, ρ the air density, and c_p the specific heat at constant pressure. For a stable condition, there is a negative heat flux $q<0$, so $L>0$ and vice versa. For the neutral condition (adiabatic) $q=0$, and hence $L = \infty$. The constant value of $\frac{kz}{u_*}\frac{d\bar{u}}{dz}$ in the neutral conditions (Eqn. (23)) is now replaced by an undetermined function $\phi(\zeta)$ of the non-dimensional variable ζ,

$$\text{i.e.} \qquad \frac{kz}{u_*}\frac{d\bar{u}}{dz} = \phi(\zeta) \tag{28a}$$

where $\zeta = \frac{z}{L}$.

Since for adiabatic conditions $\zeta = 0$, it follows $\phi(0) = 1$. Thus for the case $L \neq \infty$, the Lagrangian similarity hypothesis should be introduced as follows:

"The statistical properties of the velocity of a marked fluid particle at time t after release at height h above the ground depend only on u_*, L and t, provided that $t >> t_1$, where t_1 is expected to be the order of h/u_*."

B. Applications

1. Consequences of the Lagrangian similarity hypothesis.

For a marked fluid particle is released at $t = o$ from $z = h$, in neutrally stable conditions, after $t >> h/u_*$, as a consequence of Lagrangian similarity hypothesis, we have the following equations based on dimensional grounds:

$$\frac{d^2\bar{x}}{dt^2}, \quad \frac{d^2\bar{y}}{dt^2}, \quad \frac{d^2\bar{z}}{dt^2} \propto \frac{u_*}{t + t_1/u_*} \qquad (29) - (31)$$

Eqn. (29) in equality form

$$\frac{d^2\bar{x}}{dt^2} = \frac{a u_*}{t + t_1} \qquad (32)$$

where a is a dimensionless constant, and $t_1 = \frac{h}{u_*}$.

Integration of (32) gives

$$\frac{d\bar{x}}{dt} = a u_* \ln \frac{t+t_1}{t_0+t_1} \qquad (33)$$

where t_o is the instant at which the particle has zero mean horizontal velocity.

Assume the mean flow does not vary in the y direction, then because of symmetry

$$\frac{d^2\bar{y}}{dt^2} = \frac{d\bar{y}}{dt} = 0 \qquad (34)$$

By proper choice of the origin of the coordinates, then $\bar{y} = o$.

The vertical displacement of the marked fluid particle cannot have an infinite rate of change at any time, so that the proportionality constant in Eqn. (31) must be zero.

$$\frac{d\bar{z}}{dt} = b u_* \qquad (35)$$

or

$$\bar{z} = b u_* (t + t_2) \qquad (36)$$

where b is another dimensionless constant. Batchelor estimated the value b to be about $0.1 \sim 0.2$, and Cermak (1963) found that for $b = 0.1$ the theory was in fairly good agreement with the limited experimental data. Eqn. (27), the mean

velocity at a point, and Eqn. (33), velocity of a particle are both logarithmic functions of height and time of flight, respectively. This points to a connection between the constants a, t_2, Z_o, etc., in Eqns. (27) and (33). As mentioned before, a relation between the Lagrangian and Eulerian fields is usually difficult to obtain, but the Lagrangian similarity hypothesis makes it possible here.

The mean spread of a particle at time t should be equal to the mean speed of the fluid at some constant times the mean height of the particle, viz.,

$$\frac{d\bar{x}}{dt} = \left[\bar{u}(z)\right]_{z=c\bar{z}} = \frac{u_*}{k} \ln \frac{c\bar{z}}{z_o} \tag{38}$$

where c is a dimensionless constant. In view of the decrease of $\frac{d\bar{u}}{dz}$ with height, c should be less than unity. Substitute of $\frac{d\bar{x}}{dt}$ from Eqn. (33), and $\bar{z}$ from Eqn. (36), we have

$$a \ln \frac{t+t_1}{t_o+t_1} = \frac{1}{k} \ln \frac{b c u_* (t+t_2)}{z_o} \tag{39}$$

For continuous t, Eqn. (39) implies that

$$a = \frac{1}{k} \quad , \quad t_1 = t_2 \quad , \quad b c u_* (t_o + t_1) = z_o \tag{40}$$

These relations may be substituted into Eqns. (36) and (38) to give

$$\bar{z} = b u_* (t + t_1) \tag{41}$$

$$\frac{d\bar{x}}{dt} = \frac{u_*}{k} \ln \frac{b c u_* (t+t_1)}{z_o} = \frac{u_*}{k} \ln \frac{c\bar{z}}{z_o} \tag{42}$$

The relation between $\bar{x}$ and $\bar{z}$ is given by

$$\frac{d\bar{x}}{d\bar{z}} = \frac{1}{bk} \ln \frac{c\bar{z}}{z_o} \tag{43}$$

Integration of (43) gives

$$\tilde{x} = \frac{1}{bk}\left(\tilde{z}\ln\frac{c\tilde{z}}{z_o} - \tilde{z} + A\right) \tag{44}$$

where A is another constant. The physical meaning of Eqn. (44) is that the Eqn. (44) is an equation of the path of a hypothetical particle which moves with velocity equal to the mean velocity of a marked fluid particle, or the equation to the center-line of the cloud of marked fluid particles released by some continuous sources.

In order to determine the constant A, consider the mean velocity of a particle released at the height h at t = o has $\bar{u}(h)$, o, and o in the x, y, z direction respectively. After a period of time, $t \sim \frac{h}{u_*}$ for the particle to forget its position of release,

at $\tilde{z}=h$ then $\tilde{x} = \bar{u}(h)\cdot\frac{h}{u_*}$

therefore (45)

$$\frac{h}{u_*}\bar{u}(h) = \frac{1}{bk}\left(h\ln\frac{ch}{z_o} - h + A\right)$$

and from Eqn. (27), we get

$$A = h\left\{(b-1)\ln\frac{h}{z_o} + 1 - \ln c\right\} \tag{46}$$

For $\frac{h}{z_o} >> 1$, then A < O because b-1 < O.

Consequently, increase of h leads to a larger value of $\tilde{z}$ at a given value of $\tilde{x}$. The physical meaning of this consequence is that a smoke cloud from a certain source has a higher center-line of the cloud for a higher source, i.e., h. This is shown in Fig. 6.

Substituting A into Eqn. (44) gives

$$bk\frac{\tilde{x}}{h} = \frac{\tilde{z}}{h}\ln\frac{\tilde{z}}{h} + \left(\frac{\tilde{z}}{h}-1\right)\left(\ln\frac{ch}{z_o}-1\right) + b\ln\frac{h}{z_o} \tag{47}$$

in the case of ground level source, h → o. A = O

and Eqn. (44) becomes

$$bk\,\tilde{x} = \tilde{z}\ln\frac{c\tilde{z}}{z_o} - \tilde{z} \tag{48}$$

2. The mean concentrations at ground level for different sources.

The Lagrangian similarity hypothesis may be applied to predict the mean concentration of dispersing substances. We shall consider three different kinds of sources, namely, the instantaneous point source, continuous point source, and continuous line source. Without loss of generality, all the considerations will be restricted to steady state, ground level source.

(i) Instantaneous point source

The probability density function ψ that a particle diffusion on the ground level will reach a distance $r=(x^2+y^2+z^2)^{\frac{1}{2}}$ from its origin. The average position must be a universal function of $\frac{x-\bar{x}}{\bar{z}}$, $\frac{y}{\bar{z}}$, $\frac{z-\bar{z}}{\bar{z}}$. According to the Lagrangian similarity hypothesis, the average concentration of the marked fluid particle release instantaneous from the coordinate origin must be, on the dimensional ground,

$$C_{ips}(x,y,z)=\frac{Q_i}{\bar{z}^3}\psi\left(\frac{x-\bar{x}}{\bar{z}},\frac{y}{\bar{z}},\frac{z-\bar{z}}{\bar{z}}\right) \tag{49}$$

where Q_i is the strength of the instantaneous point source, with dimension of mass. The ground level concentration is at $y=z=0$,

$$C_{ips}(x,0,0)=\frac{Q}{\bar{z}^3}\psi\left(\frac{x-\bar{x}}{\bar{z}},0,-1\right) \tag{50}$$

(ii) Continuous point source

For a continuous point source, the marked fluid particle is emitted steady from the source, the probability of finding a marked fluid particle at x, y, z at any time is found by a time integration from o to ∞,

$$C_{cps}(x,y,z)=W_i\int_0^\infty\frac{1}{\bar{z}^3}\psi\left(\frac{x-\bar{x}}{\bar{z}},\frac{y}{\bar{z}},\frac{z-\bar{z}}{\bar{z}}\right)dt \tag{51}$$

where W_i is the strength of the continuous point source with dimension of mass per unit time.

The mean height of the particle $\bar{z}$ is related to t by Eqn. (41). By the change of variable $dt = \frac{1}{b u_*} d\bar{z}$, we have

$$C_{cps}(x, y, z) = \frac{W_i}{b u_*} \int_0^\infty \frac{1}{\bar{z}^3} \psi\left(\frac{x-\bar{x}}{\bar{z}}, \frac{y}{\bar{z}}, \frac{z-\bar{z}}{\bar{z}}\right) d\bar{z} \tag{52}$$

from the Eqn. (43), $d\bar{z} = \frac{\sigma k}{\ln \frac{c\bar{z}}{z_0}} d\bar{x}$

$$\therefore C_{cps}(x, y, z) = \frac{W_i k}{u_*} \int_0^\infty \psi\left(\frac{x-\bar{x}}{\bar{z}}, \frac{y}{\bar{z}}, \frac{z-\bar{z}}{\bar{z}}\right) \frac{1}{\bar{z}^3 \ln \frac{c\bar{z}}{z_0}} d\bar{x} \tag{53}$$

at ground level $y = z = 0$

$$\therefore C_{cps}(x, 0, 0) = \frac{-W_i k}{u_*} \int_{x/\bar{z}}^{-\infty} \psi\left(\frac{x-\bar{x}}{\bar{z}}, 0, -1\right) \frac{1}{\bar{z}^2 \ln \frac{c\bar{z}}{z_0}} d\left(\frac{x-\bar{x}}{\bar{z}}\right) \tag{54}$$

since the function ψ is expected to have a sharp maximum at $x = \bar{x}$, the Laplace method of the asymptotic integration may be applied (Carrier, et. al., 196 in this case. The form of function ψ need not be known. As $x \to \infty$, we have

$$\begin{aligned} C_{cps}(x, 0, 0) &= -\frac{W_i k}{u_*} \int_\infty^\infty \psi(\eta_x, 0, -1) \frac{1}{\bar{z}^2 \ln \frac{c\bar{z}}{z_0}} d\eta_x \\ &= \frac{W_i k}{u_*} \left\{ \bar{z}^2 \ln \frac{c\bar{z}}{z_0} \right\}^{-1}_{\bar{x}=x} \int_{-\infty}^\infty \psi(\eta_x, 0, -1) d\eta_x \end{aligned} \tag{55}$$

where $\eta_x = \frac{x-\bar{x}}{\bar{z}}$

as $\bar{x} \to \infty$, $\bar{z}/\bar{x} \to 0$

From Eqn. (48), we have

$$C_{cps}(x, 0, 0) = \frac{W_i}{b^2 k u_* x^2} \left\{ \ln \frac{c\bar{z}}{z_0} \right\}_{\bar{x}=x} \int_{-\infty}^\infty \psi(\eta_x, 0, -1) d\eta_x \tag{56}$$

$$\sim \frac{W_i}{u_* x^2} \left\{ \ln \frac{c\bar{z}}{z_0} \right\}_{\bar{x}=x}$$

(iii) Continuous line source

The concentration distribution due to a continuous line source is obtained from Eqn. (51) by integrating with respect to y over the range from - ∞ to ∞.

$$C_{cls}(x,z) = \frac{V_i}{bU_z} \int_{-\infty}^{\infty}\int \psi\left(\frac{x-\bar{x}}{\bar{z}}, \frac{y}{\bar{z}}, \frac{z-\bar{z}}{\bar{z}}\right) \frac{1}{\bar{z}^3} d\bar{z}\, dy \tag{57}$$

where V_i is the rate of emission per unit length of the line source, with dimension of mass per unit time, per unit length. By the transformation

$$d\bar{z} = \frac{b\,k}{\ln \frac{c\bar{z}}{z_0}} d\bar{x}$$

we have,

$$C_{cls}(x,z) = \frac{V_i k}{U_*} \int_{-\infty}^{\infty}\int \psi\left(\frac{x-\bar{x}}{\bar{z}}, \frac{y}{\bar{z}}, \frac{z-\bar{z}}{\bar{z}}\right) \frac{1}{\bar{z}^2 \ln \frac{c\bar{z}}{z_0}} dy\, d\bar{x} \tag{58}$$

Let $\frac{x-\bar{x}}{\bar{z}} = \eta_x$, $\frac{y}{\bar{z}} = \eta_y$, $\frac{z-\bar{z}}{\bar{z}} = \eta_z$

then

$$C_{cls}(x,z) = -\frac{V_i k}{U_*} \int_{\infty}^{-\infty}\int_{-\infty}^{\infty} \psi(\eta_x, \eta_y, \eta_z) \frac{1}{\ln \frac{c\bar{z}}{z_0}} d\eta_y\, d\eta_x \tag{59}$$

as $x \to \infty$, and at ground level.

$$C_{cls}(x,0) = \frac{V_i k}{U_*} \left\{\bar{z} \ln \frac{c\bar{z}}{z_0}\right\}^{-1}_{\bar{x}=x} \int_{\infty}^{\infty}\int_{-\infty}^{\infty} \psi(\eta_x, \eta_y, -1)\, d\eta_y\, d\eta_x \tag{60}$$

As $\bar{x} \to \infty$, the last term in Eqn. (48) becomes negligible,

$$\text{So} \quad C_{cls}(x,0) \sim \frac{V_i}{U_* x} \tag{61}$$

3. Comparison of Theoretical Prediction and Experimental Observations.

Sutton (1953), Cermak (1963), Gifford (1962) quote the results of some measurements which may be compared with the theory. It was found that the concentration varied as $x^{-1.76}$ for a continuous point

source and $x^{-0.9}$ for a continuous line source. It appears then that the Lagrangian similarity hypothesis does make possible a satisfactory assessment of the effect of the inhomogeneity of the turbulence on the diffusion from sources and that the predicted ground level mean concentrations far downwind from the source of instantaneous point or continuous point or continuous line source do in fact agree roughly with experimental observations (see Table III).

IV. LAGRANGIAN SIMILARITY HYPOTHESIS FOR CHEMICALLY REACTING DIFFUSION

A. Theory

The Lagrangian similarity hypothesis proposed by Batchelor is limited to the non-reacting case. In the case of diffusion with chemical reaction, the hypothesis is generally no longer applicable. However, for a slow chemical reaction, the hypothesis can be extended to the chemically reacting case. In the following derivation the ideas are mainly due to FRIEDLANDER and SEINFELD, and we shall follow their method to formulate the theory.

Let us assume that the Eqn. (49) of the instantaneous point source can be used in the case of a reacting pollutant but with Q_i a function of time. This assumption appears reasonable if the chemical reaction processes are slow compared with the mixing process, so that Q_i is slowly varying function of time. A more quantitative criterion can be obtained by an examination of the equation of conservation of species (Eqn. (3)):

$$\frac{\partial \bar{c}_i}{\partial t} + \vec{u}_R \cdot \vec{\nabla} \bar{c}_i = - \vec{\nabla} \cdot \overline{c_i' \vec{u}'} + \bar{r}_i \tag{62}$$

Where the velocity $\vec{u}_R$ is measured relative to the velocity of the average cloud position, and all distances are measured relative to cloud center. According to the Lagrangian similarity hypothesis for the non-reacting case, the average concentration at any point in the cloud at time t after ground level release depends on distance from average position and on the vertical spread. Thus on dimensional grounds,

$$\bar{C}_i = \frac{Q_i}{\bar{z}^3} \psi(\eta_x, \eta_y, \eta_z) \tag{49}$$

for instantaneous point source.

FRIEDLANDER and SEINFELD (1969) assumed that the same form can be used in the case of reacting pollutant but with Q_i a function of time. The assumption is justified if the chemical reaction processes are slow compared

with the mixing process, so that Q_i is a slowly varying function of time. It is reasonable thus to assume the similarity form of the average chemical reaction rate $\bar{r}_i$ as

$$\bar{r}_i = \frac{1}{\bar{z}^3} \frac{dQ_i(t)}{dt} f_i(\eta_x, \eta_y, \eta_z, t) \tag{63}$$

where f_i is a probability density function depends not only on η_x, η_y, η_z but also on time t.

There seems to be no reason why the velocity relative to the cloud center, $\vec{u}_R$ in the x, y, z direction at time t should be equal to the mean speed of a particle $\frac{d\bar{z}}{dt}$, but it must be equal to the mean speed of a particle $\frac{d\bar{z}}{dt}$ times some probability function F_x, F_y, F_z, where F_x, F_y, F_z is a function of η_x, η_y, and η_z only,

i.e., $$\vec{u}_R = \frac{d\bar{z}}{dt} \vec{F}(\eta_x, \eta_y, \eta_z) \tag{64}$$

The turbulent mass flux $\overline{\vec{u}' c_i'}$ appearing in Eqn. (62) must be related to $\bar{c}_i$ or its gradient (eddy diffusivity) if Eqn. (62) is to be solved. Assuming on dimensional grounds that the turbulent mass flux is given by

$$\overline{c_i' \vec{u}'} = \bar{c}_i \frac{d\bar{z}}{dt} \vec{G}(\eta_x, \eta_y, \eta_z) \tag{65}$$

where $\vec{G}$ is a probability density function in the x, y, z directions, substitution of Eqns. (63) - (65) into Eqn. (62) gives

$$\frac{\partial \bar{c}_i}{\partial t} + \frac{d\bar{z}}{dt} \vec{F} \cdot \vec{\nabla} \bar{c}_i = - \vec{\nabla} \cdot \bar{c}_i \frac{d\bar{z}}{dt} \vec{G} + \frac{1}{\bar{z}^3} \frac{dQ_i}{dt} f_i$$

$$\frac{\partial \bar{C}_i}{\partial t} = \frac{1}{\bar{z}^3}\frac{dQ_i}{dt}\cdot\psi - 3\frac{Q_i}{\bar{z}^4}\frac{d\bar{z}}{dt}\psi$$

$$\frac{d\bar{z}}{dt}\vec{F}\cdot\vec{\nabla}C_i = \frac{d\bar{z}}{dt}\left(\vec{F}\cdot\vec{\nabla}\frac{Q_i}{\bar{z}^3}\psi\right)$$

$$= \frac{d\bar{z}}{dt}\cdot\frac{Q_i}{\bar{z}^4}\left(\vec{F}\cdot\vec{\nabla}_\eta\psi\right)$$

$$\vec{\nabla}\cdot\bar{C}_i\frac{d\bar{z}}{dt}\vec{G} = \frac{d\bar{z}}{dt}\left\{\left(\vec{\nabla}\bar{C}_i\cdot\vec{G}\right)+\bar{C}_i\left(\vec{\nabla}\cdot\vec{G}\right)\right\}$$

$$= \frac{d\bar{z}}{dt}\left\{\left(\vec{\nabla}_\eta\psi\cdot\vec{G}\right)+\left(\vec{\nabla}_\eta\cdot\vec{G}\right)\right\}\frac{Q_i}{\bar{z}^4}$$

so

$$\frac{1}{\bar{z}^3}\frac{dQ_i}{dt}\psi - 3\frac{Q_i}{\bar{z}^4}\frac{d\bar{z}}{dt}\psi + \frac{1}{\bar{z}^4}\frac{d\bar{z}}{dt}Q_i\left(\vec{F}\cdot\vec{\nabla}_\eta\psi\right)$$

$$+ \frac{1}{\bar{z}^4}\frac{d\bar{z}}{dt}Q_i\left\{\left(\vec{\nabla}_\eta\psi\cdot\vec{G}\right)+\left(\vec{\nabla}_\eta\cdot\vec{G}\right)\right\} - \frac{1}{\bar{z}^3}\frac{dQ_i}{dt}f_i = 0$$

Dividing by $\frac{Q_i}{\bar{z}^4}\frac{d\bar{z}}{dt}$:

$$\frac{\frac{1}{Q_i}\frac{dQ_i}{dt}}{\frac{1}{\bar{z}}\frac{d\bar{z}}{dt}}\left(\psi - f_i\right) - 3\psi + \left(\vec{F}\cdot\vec{\nabla}_\eta\psi\right) + \left(\vec{\nabla}_\eta\psi\cdot\vec{G}\right) + \left(\vec{\nabla}_\eta\cdot\vec{G}\right) = 0 \qquad (66)$$

Similarity exists if a differential equation (66) is a function of η_x, η_y, η_z only. There is still a term $\frac{\frac{1}{Q_i}\frac{dQ_i}{dt}}{\frac{1}{\bar{z}}\frac{d\bar{z}}{dt}}(\psi - f_i)$ which is not a function of η_x, η_y, η_z, but a function of time only. Strictly speaking the similarity proposed in Eqn. (63) - (65) does not result in a similarity solution. In other words, the similarity does not exist. However, if the term $\frac{\frac{1}{Q_i}\frac{dQ_i}{dt}}{\frac{1}{\bar{z}}\frac{d\bar{z}}{dt}}$ is suppressed or less significant compared to the other terms, then the similarity does exist in an approximate manner. Therefore, we may claim the similarity exists if

$$\left|\frac{\frac{1}{Q_i}\frac{dQ_i}{dt}}{\frac{1}{\bar{z}}\frac{d\bar{z}}{dt}}\right| \ll 1$$

and the functions $\psi(\vec{\eta})$, $\frac{F_x}{\eta_{x_1}}\frac{F_y}{\eta_{y_1}}\frac{F_z}{\eta_{z_1}}, \frac{G_x}{\eta_{x_1}}\frac{G_y}{\eta_{y_1}}, \frac{G}{\eta_z}$ are of order unity. The measure of the spread of the cloud of contaminant in the vertical direction about its center of mass is $\sum_z$, where

$$\sum_z^2 = \overline{(z-\bar{z})^2} = \int_{-\infty}^{\infty}\int\int (z-\bar{z})^2 \bar{C}_i(x,y,z,t)\, dx\, dy\, dz$$

define $$C_*(x,z,t) = \int_{-\infty}^{\infty} \bar{C}_i(x,y,z,t)\, dy$$

then $$\sum_z^2 = \int_{-\infty}^{\infty}\int (z-\bar{z})^2 C_*\, dx\, dz$$

It has been shown by Chatwin (1968) that

$$\int_{-\infty}^{\infty} C_*\, dx = \frac{1}{bU_*t}\exp\left(-\frac{z}{bU_*t}\right)$$

Hence

$$\sum_z^2 = \int_0^{\infty} \frac{(z-bU_*t)^2}{bU_*t}\exp\left(-\frac{z}{bU_*t}\right)dz$$

$$= b^2U_*^2t^2 = \bar{z}^2$$

so that

$$\sum_z = \bar{z}$$

The fractional rate of expansion of the cloud $\frac{1}{\sum_z}\frac{d}{dt}\sum_z$ is, therefore, equal to $\frac{1}{\bar{z}}\frac{d\bar{z}}{dt}$. The above criterion of the extent of similarity shows that for the similarity solution to apply, the fractional rate of change of material in the cloud due to chemical reactions must be small compared with the fractional rate of expansion of the cloud. There may be other circumstances under which the similarity hypothesis applied to a reacting system, but at the present time the above assertion may be taken as a challenge for further testing either experimentally or theoretically.

B. Applications

1. Development and generalization of Lagrangian similarity to chemically reacting diffusion of different sources.

The chemical reaction rate for component i can be written in terms of the chemical reaction rates for the p reactions involving n chemical species as follows

$$r_i = \sum_{j=1}^{p} \nu_{ij} J_j \tag{68}$$

where J_j is the rate of the jth reaction and ν_{ij} is the stoichiometric coefficient for component i in the jth reaction. In other words, there are n chemical species involving in p chemical reactions,

$$\begin{aligned}
&\nu_{11} M_1 + \nu_{21} M_2 + \cdots + \nu_{n1} M_n = 0 \quad ; \quad J_1 \\
&\nu_{12} M_1 + \nu_{22} M_2 + \cdots + \nu_{n2} M_n = 0 \quad ; \quad J_2 \\
&\vdots \qquad\qquad\qquad\qquad\qquad\qquad\quad \vdots \\
&\nu_{1p} M_1 + \nu_{2p} M_2 + \cdots + \nu_{np} M_n = 0 \quad ; \quad J_p
\end{aligned} \tag{69}$$

Chemical reaction rate of jth reaction can be expressed in the form

$$J_j = k_j \prod_{k=1}^{n} C_k^{\alpha_{kj}} \tag{70}$$

where α_{kj} is the order of reaction of species k in the jth reaction. If the fluctuating reaction term r_i' is negligible, Eqn. (68) can be written as

$$\bar{r}_i = \sum_{j=1}^{p} \nu_{ij} k_j \prod_{k=1}^{n} C_k^{\alpha_{kj}} \tag{71}$$

In the following, we shall apply the Lagrangian similarity hypothesis to different sources(Seinfeld, 1969).

(i) Instantaneous point source

For the case of an instantaneous point source, the similarity form for C_i must also be consistent with the following condition

$$\frac{dQ_i}{dt} = \int_{-\infty}^{\infty}\int\int \bar{r}_i \, dx\, dy\, dz \tag{72}$$

where $Q_i(t)$ = mass of species at time t

From Eqn. 71, we get

$$\frac{dQ_i}{dt} = \int_{-\infty}^{\infty}\int\int \sum_{j=1}^{p} \nu_{ij} k_j \prod_{k=1}^{n} C_k^{\alpha_{kj}} \, dx\, dy\, dz \tag{73}$$

Lagrangian similarity hypothesis for chemically reacting diffusion implies

$$C_k(x, y, z, t) = \frac{Q_k(t)}{\bar{z}^3} \psi\left(\frac{x-\bar{x}}{\bar{z}}, \frac{y}{\bar{z}}, \frac{z-\bar{z}}{\bar{z}}\right) \tag{74}$$

using the relation in Eqn. 73, then

$$\frac{1}{\bar{z}^3}\frac{dQ_i}{dt} = \sum_{j=1}^{p} \nu_{ij} k_j A_j \prod_{k=1}^{n} \left(\frac{Q_k}{\bar{z}^3}\right)^{\alpha_{kj}} \tag{75}$$

Where

$$A_j = \int_{-1}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \prod_{k=1}^{n} \psi^{\alpha_{kj}}\, d\eta_x\, d\eta_y\, d\eta_z = \int_{-1}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^{\sum_{k=1}^{n}\alpha_{kj}}\, d\eta_x\, d\eta_y\, d\eta_z \tag{76}$$

In this way, the diffusion and chemical reaction effects are partially uncoupled. The set of nonlinear, coupled, second order partial differential equation (Eqn. 62) has been reduced to a set of nonlinear, coupled, first order ordinary differential equations suitable for numerical evaluation. Eqn. (75) corresponds to the kinetic expression for variable volume batch reactor (VVBR) and is related to chemical reactor models often studied in chemical engineering (Denbigh, 1965). The term $Q_i/\bar{z}^3$ is equivalent to the concentration of component i in the reactor and $\bar{z}^3$ to the reactor volume.

The ground level concentration is given by the following relation when

$y = z = 0$, $x = \bar{x}$

$$C_{i0} = a\,\frac{\theta_i}{\bar{z}^3} \tag{77}$$

where a is a constant equal $\psi(0, 0, -1)$.

Since $\bar{z}$, the mean position of the cloud above ground, increases monotonically with time as cloud expands. The concentration at ground level of a non-reacting species decreases continuously as cloud expands. For a species generating by chemical reaction, such as NO_2, or O_3 in the case of photochemical smog, Q_i increases with time for at least some portion of the cloud trajectory. In this case, a maximum concentration can be expected.

(ii) Continuous point source

The coordinate system employed in the mathematical analysis is shown below (Fig. 7),

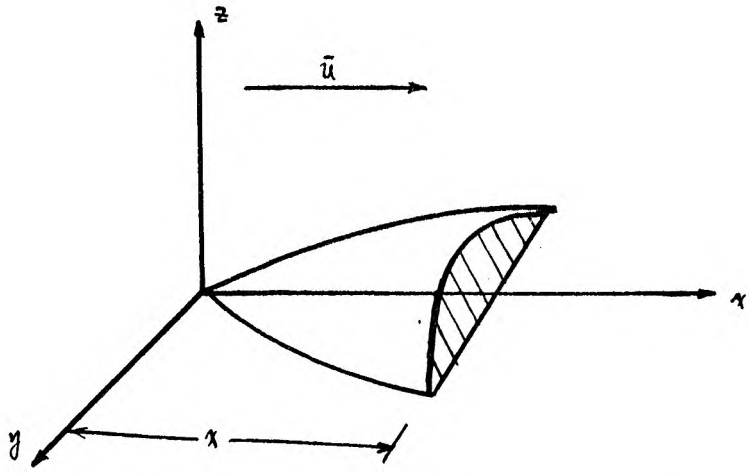


Fig. 7. Coordinate System of Continuous Point Source and Continuous Line Source

For any plane at constant x the continuity condition holds:

$$W_i(x) = \int_0^\infty \int_{-\infty}^{\infty} \bar{u}(z)\, \bar{C}_i(x, y, z)\, dy\, dz \tag{78}$$

where $W_i(x)$ = mass of species i per unit time crossing a plane at x. Because of chemical reaction, $W_i(x)$ is no longer a constant but a function of x.

Differentiate Eqn. (78) with respect to x, we have

$$\frac{dW_i(x)}{dx} = \int_0^\infty \int_{-\infty}^{\infty} \bar{u}(z)\, \frac{\partial \bar{C}_i}{\partial x}\, dy\, dz \tag{79}$$

Now, from the equation of conservation of species, Eqn. (62), with neglect of diffusion in the x direction,

$$\bar{u}(z)\frac{\partial \bar{C}_i}{\partial x} = \frac{\partial}{\partial y}\left(K_y \frac{\partial \bar{C}_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial \bar{C}_i}{\partial z}\right) + \bar{r}_i \tag{80}$$

Thus,
$$\frac{dW_i(x)}{dx} = \int_0^\infty \int_{-\infty}^{\infty} \left[\frac{\partial}{\partial y}\left(K_y \frac{\partial \bar{C}_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial \bar{C}_i}{\partial z}\right) + \bar{r}_i\right] dy\, dz \tag{81}$$

The boundary conditions are

$$K_y \frac{\partial \bar{C}_i}{\partial y} = 0 \qquad \text{at} \qquad y = \pm\infty$$

$$K_z \frac{\partial \bar{C}_i}{\partial z} = 0 \qquad \text{at} \qquad z = 0, \infty$$

By using these boundary conditions in the integration of the first two terms at the right hand side of Eqn. (81), we have

$$\frac{d\,W_i(x)}{dx} = \int_0^\infty \int_{-\infty}^{\infty} \bar{r}_i \, dy\, dz \tag{82}$$

By applying the Lagrangian similarity hypothesis for the reacting case, from Eqn. (52),

$$(C_i)_{eps}\,(x,y,z) = \frac{W_i(x)}{b u_*} \int_0^\infty \frac{1}{\bar{z}^3} \psi(\eta_x, \eta_y, \eta_z)\, d\bar{z}$$

$$= W_i(x)\, \Lambda(\eta_x, \eta_y, \eta_z) \tag{83}$$

where

$$\Lambda(\eta_x, \eta_y, \eta_z) = \frac{1}{b u_*} \int_0^\infty \frac{1}{\bar{z}^3} \psi(\eta_x, \eta_y, \eta_z)\, d\bar{z} \tag{84}$$

For a chemical reaction system given by Eqn. (69), and chemical reaction rate

$$\bar{r}_i = \sum_{j=1}^{p} \nu_{ij} k_j \prod_{k=1}^{n} \bar{C}_k^{\alpha_{kj}}$$

$$= \sum_{j=1}^{p} \nu_{ij} k_j \Lambda^{\sum_{k=1}^{n} \alpha_{kj}} \prod_{k=1}^{n} W_i(x)^{\alpha_{kj}} \tag{85}$$

substituting Eqn. (85) into Eqn. (82), then

$$\frac{d\,W_i(x)}{dx} = \sum_{j=1}^{p} \nu_{ij} k_j B_j(x) \prod_{k=1}^{n} W_k(x)^{\alpha_{kj}} \tag{86}$$

where

$$B_j(x) = \int_0^\infty \int_{-\infty}^{\infty} \Lambda^{\sum_{k=1}^{n} \alpha_{kj}}\, dy\, dz \tag{87}$$

In the same way as in the instantaneous point sources, the partial differential equation has been partially uncoupled to a set of ordinary differential equations. The ground level concentration is easy to obtain by setting $y = z = 0$ in Eqn. (83).

(iii) Continuous line source

In the case of continuous line source, the concentration is no longer a function of y . In a sense, this is much easier than the case of continuous point source. The analysis of the diffusion from a continuous line source based on the Lagrangian similarity hypothesis for chemically reacting is similar to the previous discussions of continous point source.

Refer to the coordinate system given in (ii), at any plane x = constant downwind from the source, the continuity condition implies

$$V_i(x) = \int_0^\infty \bar{u}(z)\, \bar{C}_i(x, z)\, dz \tag{88}$$

where $V_i(x)$ is mass of species i crossing the plane at x = constant. Differentiate Eqn. (88) with respect to x :

$$\frac{dV_i(x)}{dx} = \int_0^\infty \bar{u}(z)\, \frac{\partial \bar{C}_i}{\partial x}\, dz \tag{89}$$

From the equation of the conservation of species, Eqn. (62), with negligible diffusion in the x and y directions, we have

$$\bar{u}(z)\, \frac{\partial \bar{C}_i}{\partial x} = \frac{\partial}{\partial z}\left(K_z \frac{\partial \bar{C}_i}{\partial z}\right) + \bar{r}_i \tag{90}$$

substituting into Eqn. (89), then

$$\frac{dV_i(x)}{dx} = \int_0^\infty \left[\frac{\partial}{\partial z}\left(K_z \frac{\partial \bar{C}_i}{\partial z}\right) + \bar{r}_i\right] dz \tag{91}$$

Then boundary condition $K_z \frac{\partial \bar{C}_i}{\partial z} = 0$ at $z = 0, \infty$ implies the first term of the integration of Eqn. (91) is zero.

Therefore $$\frac{d V_i(x)}{dx} = \int_0^\infty \bar{r}_i \, dz \tag{92}$$

By applying Lagrangian similarity hypothesis for chemically reacting diffusion,

$$(C_i)_{cls}(x,z) = \frac{V_i(x)}{b U_*} \int_{-\infty}^{\infty}\int \frac{\psi}{\bar{z}^3}(\eta_x, \eta_y, \eta_z)\, d\eta\, d\bar{z}$$

$$= V_i(x)\Omega(\eta_x) \tag{93}$$

where $$\Omega(\eta_x) = \frac{1}{b U_*} \int_{-\infty}^{\infty}\int \frac{\psi}{\bar{z}^3}(\eta_x, \eta_y, \eta_z)\, d\eta\, d\bar{z} \tag{94}$$

For a chemical reaction system given by Eqn. (69) and with reaction rate given by Eqn. (71), then

$$\frac{d V_i(x)}{dx} = \sum_{j=1}^{p} \nu_{ij} k_j C_j(x) \prod_{k=1}^{n} V_k(x)^{\alpha_{kj}} \tag{95}$$

where $$C_j(x) = \int_0^\infty \Omega^{\sum_{k=1}^{n} \alpha_{kj}} \, dz \tag{96}$$

Again, the partial differential equation has been partially uncoupled to an ordinary differential equation.

(iv) Relationship among the three different sources and their assumptions.

The probability of finding the marked fluid particle in a neighborhood of the point x, y, z at time t is $\psi(x, y, z, t)$.
In our three sources, our assumption is that ψ is invariant with respect to t, but a function of η_x, η_y , and η_z only.

For an instantaneous point source, the mean concentration is given by

$$[C_i(x,y,z,t)]_{ips} = \frac{Q_i(t)}{\bar{z}^3} \psi(\eta_x, \eta_y, \eta_z) \tag{97}$$

For a continuous point source, the mean concentration is found by an integration of instantaneous point source for t from o to ∞. The concentration is no longer a function of time t.

$$\left[C_i(x,y,z)\right]_{cps} = W_i(x)\int_0^\infty \frac{1}{\bar{z}^3}\psi(\eta_x,\eta_y,\eta_z)\,dt \tag{98}$$

For a continuous line source, the mean concentration is found by integrating the continuous point source for y from $-\infty$ to $+\infty$. The mean concentration is therefore a function of x and z only,

$$\left[C_i(x,z)\right]_{cls} = V_i(x)\int_0^\infty\int_{-\infty}^\infty \frac{1}{\bar{z}^3}\psi(\eta_x,\eta_y,\eta_z)\,dy\,dt \tag{99}$$

Consider a sequence of instantaneous non-interacting point sources of strength ΔQ_{io}, then

$\frac{\Delta Q_i}{\Delta x}$ is the rate of emission of species i.

$$\left[C_i(x,y,z)\right]_{cps} = \int_0^\infty \frac{\Delta Q_i}{\Delta t}\frac{\psi(\eta_x,\eta_y,\eta_z)}{\bar{z}^3}\,dt \tag{100}$$

If the species i at $t = o$ is emitted Q_{io}, then $\frac{\Delta Q_{io}}{\Delta t}$ is constant, so that

$\frac{\Delta Q_i}{\Delta t} \longrightarrow W_i(x)$, a function of x only, as $\Delta t \to 0$,

$$\text{i.e.,}\quad \left[C_i(x,y,z)\right]_{cls} = \int_0^\infty W_i(x)\frac{\psi}{\bar{z}^3}\,dt \tag{101}$$

The independent variable of $\frac{\Delta Q_i}{\Delta t}$ is changed from t to x. In the Eulerian sense, $\frac{\Delta Q_i}{\Delta t}$ only changes with x. The relationship between three cases may be summarized as follows:

Type of source	I.P.S.	C.P.S.	C.L.S.
Source strength	Q_i	$W_i(x)$	$V_i(x)$
L.S.H. Form	Eqn. (97)	Eqn. (98)	Eqn. (99)

2. Applications of Lagrangian Similarity Hypothesis of Chemically Reacting Diffusion to a Bimolecular Chemical Reaction $A + B \rightarrow C$

The application of the Lagrangian similarity hypothesis to a bimolecular chemical reaction from an instantaneous point source has been shown by Friedlander and Seinfeld (1969). Since it demonstrates the application of the hypothesis effectively, it is thus proper to show their results here.

(i). Instantaneous point source.

An analytical solution can be obtained for neutral conditions when $\phi(\zeta) = \phi(0) = 1$. The solution which satisfies the initial condition $Q_c = 0$ at $\bar{z} = h$ is

$$Q_c = Q_{A0} \frac{\left\{ 1 - \exp\left\{ -\frac{A}{2b} N_S (\sigma - 1)\left(1 - h^2/\bar{z}^2\right) \right\} \right\}}{\left\{ 1 - \frac{1}{\sigma} \exp\left\{ -\frac{A}{2b} N_S (\sigma - 1)\left(1 - h^2/\bar{z}^2\right) \right\} \right\}} \tag{109}$$

where

$$N_S = \frac{k Q_{A0}}{u_* h^2} \quad ; \quad \sigma = \frac{Q_{B0}}{Q_{A0}} \tag{110}$$

The result of calculations based on Eqn. (110) are shown in Figs. 8, 9, and 10. Figures 8 shows that the dimensionless ground level concentration of product reaches a maximum near the source and then rapidly decays. For given values of σ, the ratio of reactant source strengths, highest ground level concentrations are obtained for large values of N_S, corresponding to high chemical reaction rates and low friction velocities.

In Fig. 9 and 10 it is shown that the condition $\left| \frac{1/Q_i \frac{dQ_i}{dt}}{1/\bar{z} \frac{d\bar{z}}{dt}} \right| \ll 1$ is best satisfied for large values of $\bar{z}/h$, consistent with the asymptotic nature of the original similarity hypothesis on which the analysis is based.

The ratio $\left| \frac{\frac{1}{Q_i}\frac{dQ_i}{dt}}{\frac{1}{\bar{z}}\frac{d\bar{z}}{dt}} \right|$ is greatest near the source and then falls rapidly since the chemical reaction rates are particularly sensitive to the reactant concentrations. The total quantity of product generated by the chemical reaction as $\bar{z} \to \infty$ can be calculated from Eqn. 109 and is

$$Q_{co} = Q_{AO} \frac{\left\{ 1 - \exp\left[-\frac{A}{2b} N_s (\sigma - 1) \right] \right\}}{\left\{ 1 - \frac{1}{\sigma} \exp\left[-\frac{A}{2b} N_s (\sigma - 1) \right] \right\}} \tag{111}$$

$Q_{c\infty}$ is always less than Q_{A_0} ; the maximum amount of product which would be produced in a fixed volume batch reactor ($Q_{A_0} < Q_{B_0}$). The reduction results from the quenching effect of the rapid expansion of the VVBR ($\bar{z}^3 \sim t^3$). This seems to be an important result. Not only is the concentration of the product of the chemical reaction reduced by the mixing process, but so also is the maximum attainable total quantity of product. The extent of the reduction depends on the dimensionless group N_S: small values of N_S, corresponding to low reaction rates (small k) and large mixing rates (high u_*), lead to small values of $Q_{c\infty}$. From this kind of analysis, it is possible to develop simple criteria for atmospheric contaminant levels in a reacting system. For example, if σ^{-1} and $N_S << 1$, Eq. (111) can be written approximately as

$$\frac{Q_{c_0}}{Q_{A_0}} = \frac{A k Q_{B_0}}{2 b u_* h^2} \tag{112}$$

Now assume that Q_{A_0} and Q_{B_0} represent the total amounts of pollutants A and B emitted by a source into an air basin with inversion height H. As the cloud expands to the inversion height, the total amount of product generated, $Q_{c\infty}$, will be mixed into the volume HS where S is the effective area covered by the cloud. This leads to the following result for the average concentration of product, $Q_{c\infty}/HS$, after expansion to the inversion height:

$$\frac{(Q_{c\infty}/HS)\, u_* H}{k} = \frac{A Q_{A_0} Q_{B_0}}{2 b h^2 S} \tag{113}$$

When pollutant emissions and the effective area covered by the cloud are constant, the right hand side of Eq. (113) is a constant, independent of meteorological conditions. Eq. (113) is then similar in form to a correlation proposed by Schuck, Pitts and Wan (1966) for oxidant concentration in

the Los Angeles basin. The Schuck, et.al. expression was empirically derived, based on only two sets of experimental data. The theoretical calculation given above is based on the bimolecular reaction model which is highly simplified so far as smog is concerned. Hence it cannot be claimed that the correlation is well established either on experimental or theoretical grounds. It will be interesting to see whether further studies support this observation.

(ii). Continuous Point Source and Continuous Line Source

For a bimolecular chemical reaction, Eqn. (86) leads to the following equation:

$$\frac{d\bar{W}_c(x)}{dx} = k\,B(x)\,(\bar{W}_{A0}-\bar{W}_c)\,(\bar{W}_{B0}-\bar{W}_c) \tag{114}$$

Let $\sigma = \frac{\bar{W}_{B0}}{\bar{W}_{A0}}$ $\qquad C = \frac{\bar{W}_c}{\bar{W}_{A0}}$

then $$\frac{dC}{dx} = k\,B(x)\,(1-C)(\sigma-C) \tag{115}$$

where $$B(x) = \int_0^{\infty}\int_{-\infty}^{\infty} \Lambda^2\, dy\, dz$$

at $x=0$, $C=0$

so $$\int_0^C \frac{dc}{(1-c)(\sigma-c)} = \int_0^x k\,B(x')\,dx' = D(x)$$

$$\bar{W}_c(x) = \bar{W}_{A0}\,\frac{\sigma\{1-\exp[(\sigma-1)D(x)]\}}{\{1-\sigma\exp[(\sigma-1)D(x)]\}} \qquad \sigma \neq 1 \tag{116}$$

$$\bar{W}_c(x) = \bar{W}_{A0}\,\frac{D(x)}{1+D(x)} \qquad \sigma = 1 \tag{117}$$

For a continuous line source, we will get a solution in the form of Eqns. (116) and (117). For further information about the mean concentration, a critical step is to investigate the probability density function ψ .

3. The Variable Volume Batch Reactor Model (VVBR) and the Critical Damkohler Parameter for the Formation of Smog.

We can now go on to discuss the more realistic case of the VVBR with the ultrasimplified model for chemical kinetics. Define the "effective concentration" η_i , such that

$$\eta_i = \frac{Q_i}{\bar{z}^3} \tag{118}$$

Then Eqn. (75) becomes

$$\frac{d\eta_i}{dt} + 3\,\frac{\eta_i}{\bar{z}}\frac{d\bar{z}}{dt} = \sum_{j=1}^{p} \nu_{ij} k_j A_j \prod_{k=1}^{n} \eta_k^{\alpha_{kj}} \tag{119}$$

Based on the extended Lagrangian similarity hypothesis, the vertical average velocity $\frac{d\bar{z}}{dt}$, on dimensional grounds must be proportional to the friction velocity u_* times some universal dimensionless function involving Monin-Obukhov length L (Eqn. 28):

$$\frac{d\bar{z}}{dt} = b\,u_*\,\phi(\zeta)$$

where $$\zeta = \frac{\bar{z}}{L}$$

and $\phi(\zeta)$ is a universal function of the dimensionless variable ζ . For adiabatic condition, $q_0 = 0$ and, therefore L = ∞, from which it follows that $\phi(\zeta) \to 1$ as $\zeta \to 0$.

From Eqn.(119), we have then

$$\frac{d\eta_i}{dt} = \sum_{j=1}^{p} \nu_{ij} k_j A_j \prod_{k=1}^{n} \eta_k^{\alpha_{kj}} - \frac{3\,\eta_i}{t + h/bu_*} \tag{120}$$

for a neutral case, i.e., L = ∞.

It is interesting to note that Eqn. (120) becomes the equation for the

constant volume batch reactor model (CVBR) as $h/bu_* \to \infty$. The results for various values of h/bu_* as a parameter, using the ultra-simplified chemical reaction model are shown in Fig. 11 through 14.

Photochemical smog reactions have been studied experimentally in smog chambers simulating atmospheric conditions. It is known that there is a dramatic conversion of NO to NO_2 when the radiant energy is supplied. Usually, however, these experiments are performed in a constant volume batch reactor. In the case of variable volume batch reactor, as photochemical smog in the atmosphere, the pollutants not only react with each other, they also disperse into the atmosphere. If diffusion is rapid, there may be no photochemical reactions occurring, because the reactions may be quenched due to dispersion. On the other hand, if chemical reaction controls, then the photochemical reaction will not die out even at very low concentration. It has been shown that the Lagrangian similarity hypothesis applied to the reacting case of the chemical reaction is slow compared to the atmospheric dispersion, i.e.,

$$\left| \frac{\frac{1}{Q_i}\frac{dQ_i}{dt}}{\frac{1}{\bar{z}}\frac{d\bar{z}}{dt}} \right| << 1$$

In the case of fast reactions, the Lagrangian similarity hypothesis is generally no longer applicable. But since the chemical reactions are fast, that short period of reaction time may be neglected. After the reactions are completed, the resultant products may be treated as passive contaminant in which the above theory may be again applicable.

It also was determined in the laboratory and in experiments that the consumption of reactant hydrocarbon, the rise of oxidant, etc., do not start until the conversion of NO to NO_2 is almost complete. It is thus reasonable to assert that the critical value for the formation of photochemical smog is when

$$\left(\frac{d n_{NO_2}}{dt}\right)_{\tau=0} \geq 0$$

If the above criterion is applied to Eqn. (120) then

$$\left[h/bu_*\right]_{cr} = \frac{3\, n_{NO_2}}{\sum_{j=1}^{p} \prod_{k=1}^{n} \nu_{ij} k_j A_j n_k^{\alpha_{kj}}} \tag{121}$$

The left hand side of Equation (121) corresponds to a mechanical time, τ_{mech}, and the right hand side of the equation corresponds to a chemical time, τ_{chem}. The Damköhler number is defined as the ratio τ_{mech}/τ_{chem}. Hence by Equation (121) the critical value for the formation of photochemical smog is thus that the Damköhler number is unity.

If the ultrasimplified model is a suitable kinetic model for the photochemical smog reaction, the critical value of h/bu_* is given by

$$\left[h/bu_*\right]_{cr} = \frac{3}{\alpha A_1 n_2 n_3 - \lambda A_2 n_1 n_3}$$

For $A_1 = A_2 \approx 1$,

the critical value is about 15 minutes for the initial concentrations :

$$[n_1]_o = 0.2 \text{ ppm}$$

$$[n_2]_o = 1.0 \text{ ppm}$$

$$[n_3]_o = 2.0 \text{ ppm}$$

The results are shown in Figures 11 through 14 for four different values of h/bu_*. For small values of h/bu_*, corresponding to rapid mixing, the chemical reaction is effectively quenched and the reactants rapidly dispersed. For $h/bu_* >$ 100 minutes, ozone begins to appear and the

curves assume a form typical of the constant batch reactor studies made in smog chambers (see Fig. 4).

4. Applications of Lagrangian similarity hypothesis of chemically reacting diffusion to the ultrasimplified model.

The extended Lagrangian similarity hypothesis can be applied to the ultrasimplified model for an instantaneous point source in the adiabatic conditions. The ultrasimplified model takes into account the chemical species NO, NO_2, O_3 O, RH, and R· (free radial). Steady state assumptions to 0, 0_3 and R· , results in three algebraic equations (FRIEDLANDER and SEINFELD, 1969):

$$[O] = \gamma\,[NO_2]$$

$$[O_3] = \beta\,[NO_2]/[NO]$$

$$[R\cdot] = k_4'\,[O][RH] = k_4\gamma\,[NO_2][RH]$$

For an elevated source, the extended Lagrangian similarity hypothesis gives the following equations for NO_2, NO and RH:

$$\frac{d\chi_1}{d\tau} = \frac{A}{b\zeta^6}\left(\alpha_N \chi_1\chi_2\chi_3 - \lambda_N \chi_1^2\chi_3\right)$$

$$\frac{d\chi_2}{d\tau} = -\frac{A}{b\zeta^6}\alpha_N \chi_1\chi_2\chi_3$$

$$\frac{d\chi_3}{d\tau} = -\frac{A}{b}\theta_N \chi_1\chi_3/\zeta^3 - A/b\;\mu_N \chi_1\chi_3/\chi_2$$

where

$$\alpha_N = (N_5)_3\,\alpha$$

$$\lambda_N = (N_5)_3\,\lambda$$

$$\theta_N = (N_5)_2\,\theta$$

$$\mu_N = (N_5)_1\,\mu$$

$$\chi_1 = \frac{Q_1}{Q_0}$$

$$\chi_2 = \frac{Q_2}{Q_0}$$

$$\chi_3 = \frac{Q_3}{Q_0}$$

Q_1, Q_2, Q_3 refers to the source strengths of NO_2, NO, and RH respectively. Q_0/h^2 is a reference concentration to make the concentration term dimensionless. α_N, λ_N, θ_N, μ_N are the Damkohler parameters defined by τ_{mech}/τ_{chem} . For example, $\alpha_N = \frac{h/u_*}{1/\alpha(\theta_0/h^2)^2}$. The Damkohler parameters include the effects of the following meteorological variables:

(1) solar radiation and temperature through reaction rate constants, α, λ, μ, and θ.

(2) Wind condition through friction velocity u_*.

(3) stability through L (L = ∞).

With given initial conditions and Damkohler parameters, the solution of the above differential equations is easy to obtain by numerical integration.

V. DETERMINATION OF THE PROBABILITY DENSITY FUNCTION

A. Non-Reacting Case

The turbulent diffusion of a passive (non-reacting) substance released from a source into the atmosphere was classified according to the condition under which the substance was released, viz., instantaneous point, continuous point and continuous line source. In the latter two cases, the strength may be a function of time. In the first case, the substance is completely discharged during an infinitesimal period of time. The puff of substance then begins to diffuse about its center of mass, which is moving randomly with turbulent motion existing in the atmosphere.

We shall first restrict our consideration to the instantaneous point source undergoing vertical diffusion, and we shall further assume that the horizontal diffusion in x and y directions are independent among themselves. In any instantaneous released source, we are interested mainly in discussing the distribution of substance about the center of mass. Thus, a Lagrangian description is more appropriate than an Eulerian in discussing the statistical properties of a diffusing puff.

After a period of time t when the puff was released, the shape of iso-concentration lines will be irregular and random. The point of maximum concentration will not necessarily coincide with the center of mass. If under the same conditions, a large number of experiments are performed, the center of mass of each puff will follow a different history due to non-stationary and inhomogeneous character of the larger eddies to the extent to which they are included or excluded by the finite interval over which the average is taken. However, as far as the relative distribution of substance with respect to the center of mass is concerned, the statistical properties may be almost equivalent to each other for individual puff, since the smaller eddies responsible for the relative distribution are supposed to be stationary

and homogeneous. Thus, if we take an infinite number of distributions, each observed at the same time interval after release, and if we superposed them in such a way that the centers of mass coincide with each other, and if we average over all the superposed distributions, we would then expect a rotationally symmetrical distribution of substance about the center of mass, which corresponds to the point of maximum concentration. The mean concentration is then a function of the diffusion time t and distance z from the center of mass.

The turbulent diffusion process, in general, is described by the following probability distributions:

$W_1(\underline{x}, t)\,d\underline{x}$ = probability of finding $\underline{\xi}(t)$ in the range $(\underline{x}, \underline{x}+d\underline{x})$ at time t, where $\underline{\xi}(t)$ is random coordinate of a marked fluid particle relative to the moving center of mass;

$W_2(\underline{x}_0, t_0; \underline{x}_1, t_1)\,d\underline{x}_0\,d\underline{x}_1$ = joint probability of finding $\underline{\xi}(t)$ in a range $(\underline{x}_0, \underline{x}_0+d\underline{x}_0)$ at time t_0 and in a range $(\underline{x}_1, \underline{x}_1+d\underline{x}_1)$ at the successive time t_1;

$W_3(\underline{x}_0, t_0; \underline{x}_1, t_1; \underline{x}_2, t_2)\,d\underline{x}_0\,d\underline{x}_1\,d\underline{x}_2$ = joint probability of finding $\underline{\xi}(t)$ in a range $(\underline{x}_0, \underline{x}_0+d\underline{x}_0)$ at t_0, and $(\underline{x}_1, \underline{x}_1+d\underline{x}_1)$ at t_1 and $(\underline{x}_2, \underline{x}_2+d\underline{x}_2)$ at t_2;

and so on.

The process is considered to be a discrete time process and $t_0 < t_1 < t_2 < \ldots$. The set of the above functions must satisfy the following conditions:

(i) $W_i(\underline{x}_0, t_0; \underline{x}_1, t_1; \cdots; \underline{x}_{i-1}, t_{i-1}) \geq 0 \quad \forall\ i \geq 1$

(ii) $W_i(\underline{x}_0, t_0; \cdots; \underline{x}_{i-1}, t_i) = \int\cdots\int d\underline{x}_i \cdots d\underline{x}_{n-1}\, W_n$,

since each function W_n must imply all the previous W_i, $i < n$.

$$\text{(iii)} \quad W_1(\underline{x}_n, t_n) = \int \cdots \int W_{n+1}(\underline{x}_0, t_0; \cdots; \underline{x}_n, t_n)\, d\underline{x}_0 \cdots d\underline{x}_{n-1} \tag{122}$$

For more precise information about the process we shall define the following transition probability functions:

Let $P_2(\underline{x}_1, t_1 \mid \underline{x}_0, t_0)$ = transition probability that given $\underline{x}_0$ at t_0 one finds $\underline{\xi}(t)$ in the range $(\underline{x}_1, \underline{x}_1 + d\underline{x}_1)$ at time t_1, where $t_1 > t_0$,

$P_3(\underline{x}_2, t_2 \mid \underline{x}_0, t_0; \underline{x}_1, t_1)$ = transition probability that given $\underline{x}_0$ and $\underline{x}_1$ at t_0 and t_1, respectively, one finds $\underline{\xi}(t)$ in the range $(\underline{x}_2, \underline{x}_2 + d\underline{x}_2)$ at time t_2, where $t_2 > t_1 > t_0$.

and so on.

These transition probabilities also have the following properties:

$$\text{(i)} \quad P_k(\underline{x}_{k-1}, t_{k-1} \mid \underline{x}_0, t_0; \cdots; \underline{x}_{k-2}, t_{k-2}) \geq 0$$

$$\text{(ii)} \quad \int P_k(\underline{x}_{k-1}, t_{k-1} \mid \underline{x}_0, t_0; \cdots; \underline{x}_{k-2}, t_{k-2}) = 1$$

$$\text{(iii)} \quad W_2(\underline{x}_0, t_0; \underline{x}_1, t_1) = W_1(\underline{x}_0, t_0)\, P_2(\underline{x}_1, t_1 \mid \underline{x}_0, t_0)$$

(iii) above is nothing but a definition of transition probability. By induction, it can be shown

$$W_3(\underline{x}_0, t_0; \underline{x}_1, t_1; \underline{x}_2, t_2) = W_2(\underline{x}_0, t_0; \underline{x}_1, t_1)\, P_3(\underline{x}_2, t_2 \mid \underline{x}_0, t_0; \underline{x}_1, t_1)$$

$$= W_1(\underline{x}_0, t_0)\, P_2(\underline{x}_1, t_1 \mid \underline{x}_0, t_0)\, P_3(\underline{x}_2, t_2 \mid \underline{x}_0, t_0; \underline{x}_1, t_1)$$

and

$$W_n(\underline{x}_0, t_0; \cdots; \underline{x}_{n-1}, t_{n-1}) = W_1(\underline{x}_0, t_0)\, P_2(\underline{x}_1, t_1 \mid \underline{x}_0, t_0) \times \cdots \times P_n(\underline{x}_{n-1}, t_{n-1} \mid \underline{x}_0, t_0; \cdots; \underline{x}_{n-1}, t_{n-1}) \tag{123}$$

Now, let

$Q(\underline{x}_k, t_k \mid \underline{x}_0, t_0)$ = transition probability that initially given $\underline{x}_0$ at t_0 one finds $\underline{\xi}(t)$ in the range $(\underline{x}_k, \underline{x}_k + d\underline{x}_k)$ at time t_k. This is a point function, i.e., it is irrespective of the $\underline{x}_1, \cdots, \underline{x}_{k-1}$ at corresponding time $t_1, \ldots, t_{k-1}$.

It then follows that

$$Q(\underline{x}_k, t_k \mid \underline{x}_0, t_0) = \int \cdots \int P_2(\underline{x}_1, t_1 \mid \underline{x}_0, t_0)\, P_3(\underline{x}_2, t_2 \mid \underline{x}_0, t_0; \underline{x}_1, t_1) \times \cdots \times P_{k+1}(\underline{x}_k, t_k \mid \underline{x}_0, t_0; \cdots; \underline{x}_{k-1}, t_{k-1})\, d\underline{x}_1\, d\underline{x}_2 \cdots d\underline{x}_{k-1} \tag{124}$$

Integrating Eqn.(123) for W_{n+1} over $\underline{x}_0, \underline{x}_1, \cdots, \underline{x}_{n-1}$,

then $\int \cdots \int W_{n+1}(\underline{x}_0, t_0; \cdots, \underline{x}_{n-1}, t_{n-1})\, d\underline{x}_0 d\underline{x}_1 \cdots d\underline{x}_{n-1}$

$$= \int \cdots \int W_1(\underline{x}_0, t_0)\, P_2(\underline{x}_1, t_1 \mid \underline{x}_0, t_0) \times \cdots \times P_{n+1}(\underline{x}_n, t_n \mid \underline{x}_0, t_0; \cdots; \underline{x}_n, t_n)\, d\underline{x}_0 \cdots d\underline{x}_{n-1} \tag{125}$$

In Eqn.(125), LHS = $W_1(\underline{x}_n, t_n)$ by Eqn.(122).

$$\therefore \quad W_1(\underline{x}_n, t_n) = \int W_1(\underline{x}_0, t_0)\, Q(\underline{x}_k, t_n \mid \underline{x}_0, t_0)\, d\underline{x}_0$$

For a given initial condition $W_1(\underline{x}_0, t_0)$, we still need to know $Q(\underline{x}_n, t_n | \underline{x}_0, t_0)$ to get $W_1(\underline{x}_n, t_n)$.

If we make an important assumption that the process of turbulent diffusion is a Markov process, then the problem is much simplified. The definition of Markov process is that

$$P\{\underline{x}_k, t_k | \underline{x}_0, t_0; \cdots; \underline{x}_{k-1}, t_k\} = P\{\underline{x}_k, t_k | \underline{x}_{k-1}, t_k\}$$

Therefore, Equation (124) may be written

$$Q(\underline{x}_k, t_k | \underline{x}_0, t_0) = \int \Big[\int \cdots \int P_2(\underline{x}_1, t_1 | \underline{x}_0, t_0) P_3(\underline{x}_2, t_2 | \underline{x}_0, t_0; \underline{x}_1, t_1) \times \cdots \times P_k(\cdots) d\underline{x}_0 \cdots d\underline{x}_{k-2} \Big] P_{k+1}(\underline{x}_k, t_k | \underline{x}_{k-1}, t_{k-1}) d\underline{x}_{k-1}$$

$$= \int Q(\underline{x}_{k-1}, t_{k-1} | \underline{x}_0, t_0) Q(\underline{x}_k, t_k | \underline{x}_{k-1}, t_{k-1}) d\underline{x}_{k-1} \qquad (126)$$

For a continuous time process, Eqn. (126) becomes

$$Q(\underline{x}, t | \underline{x}_0, t_0) = \int Q(\underline{x}, t | \underline{\xi}, \tau) Q(\underline{\xi}, \tau | \underline{x}_0, t_0) d\underline{\xi} \qquad (127)$$

This is the so-called Chapman-Smoluchowski-Kolmogorov equation.

For a stationary process,

$$Q(\underline{x}, t | \underline{x}_0, t_0) = P(\underline{x}_0, \underline{x}, t - t_0)$$

By choosing $t_0 = 0$, Eqn. (127) becomes

$$P(\underline{x}_0, \underline{x}, t) = \int P(\underline{\xi}, \underline{x}, t-\tau) P(\underline{x}_0, \underline{\xi}, \tau) d\underline{\xi}$$

$$P(\underline{x}_0, \underline{x}, t+\Delta\tau) = \int P(\underline{\xi}, \underline{x}, \Delta t) P(\underline{x}_0, \underline{\xi}, t) d\underline{\xi}$$

Propose $P(\underline{\xi}, \underline{x}, \Delta t) = \delta(\underline{x}-\underline{\xi}) + C(\underline{\xi}, \underline{x})\Delta t + O(\Delta t)^2$

so $P(\underline{x}_0, \underline{x}, t+\Delta t) = \int P(\underline{x}_0, \underline{\xi}, t) \{\delta(\underline{x}-\underline{\xi}) + C(\underline{\xi}, \underline{x})\Delta t + O(\Delta t)^2\} d\underline{\xi}$

$$= P(\underline{x}_0, \underline{x}, t) + \Delta t \int P(\underline{x}_0, \underline{\xi}, t) C(\underline{\xi}, \underline{x}) d\underline{\xi} + O(\Delta t^2)$$

Formally, taking the limit as $\Delta t \to 0$, then

$$\frac{\partial}{\partial t} P(x_0, x, t) = \int P(x_0, \xi, t)\, C(\xi, x)\, d\xi$$

The moments of the change in the space coordinate in a small time Δt are

$$a_n(x, \Delta t) = \int (x - \xi)^n\, P(\xi, x, \Delta t)\, dx$$

and we assume that for $\Delta t \to 0$ only the first and second moments become proportional to Δt , so that

let $$C(\xi, x) = -a(\xi)\delta'(x - \xi) + \frac{1}{2} b(\xi)\delta''(x - \xi)$$

then $$\frac{\partial P}{\partial t}(x_0, x, t) = \int_{-\infty}^{\infty} P(x_0, \xi, t)\left\{-a(\xi)\delta'(x - \xi) + \frac{1}{2} b(\xi)\delta''(x - \xi)\right\} d\xi$$

but $$\int_{-\infty}^{\infty} g(x)\,\delta'(x - \xi)\, dx = \sum_i g'(x)$$

$$\int_{-\infty}^{\infty} g(x)\,\delta''(x - \xi)\, dx = \sum_i g''(x)$$

$$\therefore \quad \frac{\partial}{\partial t} P(x_0, x, t) = -\frac{\partial}{\partial x}\left\{a(x)\, P(x_0, x, t)\right\} + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left\{b(x)\, P(x_0, x, t)\right\}, \tag{128}$$

which is the Fokker-Planck equation.

In vertical diffusion only, Eqn. (128) becomes

$$\frac{\partial}{\partial t} P_z(z_0, z, t) = -\frac{\partial}{\partial z}\left\{a(z)\, P_z(z_0, z, t)\right\} + \frac{1}{2}\frac{\partial^2}{\partial z^2}\left\{b(z)\, P(z_0, z, t)\right\} \tag{129}$$

If we assume $$a(z) = -\beta z$$

$$b(z) = 2D$$

then Eqn. (129) becomes:

$$\frac{\partial P_z}{\partial t} = \beta \frac{\partial}{\partial z}(z P_z) + D\frac{\partial^2 P_z}{\partial z^2} \tag{130}$$

By Fourier transform, the solution of Eqn.(130) is given by

$$P_z(z_0, z, t) = \frac{1}{(2\pi\sigma_z^2)^{\frac{1}{2}}} \exp\left[-\frac{(z-\bar{z})^2}{2\sigma_z^2}\right] \tag{131}$$

where $$\bar{z} = E\{z\} = z_0 \exp(-\beta t) \tag{132}$$

$$\sigma_z^2 = E\{(z-\bar{z})^2\} = \frac{D_z}{\beta_z}\left[1 - \exp(-2\beta_z t)\right] \tag{133}$$

The first equality signs of Eqns.(132) and(133) are definitions of mean and variance. The variance is the expectation of $(z-\bar{z})^2$.

By the previous assumption that there is no interaction among vertical and horizontal diffusion, then we have

$$P_x(x_0, x, t) = \frac{1}{(2\pi\sigma_x^2)^{\frac{1}{2}}} \exp\left[-\frac{(x-\bar{x})^2}{2\sigma_x^2}\right]$$

$$P_y(y_0, y, t) = \frac{1}{(2\pi\sigma_y^2)^{\frac{1}{2}}} \exp\left[-\frac{(y-\bar{y})^2}{2\sigma_y^2}\right]$$

where $$\bar{x} = x_0 \exp[-\beta_x t]$$

$$\bar{y} = y_0 \exp[-\beta_y t]$$

$$\sigma_x^2 = \frac{D_x}{\beta_x}\left[1 - \exp(-2\beta_x t)\right]$$

$$\sigma_y^2 = \frac{D_y}{\beta_y}\left[1 - \exp(-2\beta_y t)\right]$$

and therefore

$$\psi(x, y, z, t) = P_x P_y P_z$$

$$= \frac{1}{(2\pi)^{\frac{3}{2}}(\sigma_x \sigma_y \sigma_z)} \exp\left[-\left\{\frac{(x-\bar{x})^2}{2\sigma_x^2} + \frac{(y-\bar{y})^2}{2\sigma_y^2} + \frac{(z-\bar{z})^2}{2\sigma_z^2}\right\}\right] \tag{134}$$

By assuming $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \sigma^2$

Eqn.(134) becomes

$$\psi(x,y,z,t) = \frac{1}{(2\pi\sigma^2)^{\frac{3}{2}}} \exp\left[-\frac{(x-\bar{x})^2+(y-\bar{y})^2+(z-\bar{z})^2}{2\sigma^2(t)}\right] \qquad (135)$$

Eqn.(135) is exactly the form assumed by Gifford (1957). Eqn.(134) is more general, and requires information about σ_x^2, σ_y^2 and σ_z^2 from experimental results.

Although our derivation from the fundamental theory of stochastic processes has reached a form consistent with those proposed by Gifford (1957). Experiment has shown that Eulerian statistics of turbulent dispersion are not exactly Gaussian. Therefore, one must be careful not to take the applicability of the Markov theory to turbulence too literally. However, this research is clearly emphasized on practical application on engineering modeling. It is thus undoubtedly reasonable as a practical assumption for real turbulence.

B. Reacting Case and Its Applications (Proposed)

It is from the analysis in Part (A) we get a probability density function ψ consistent with experimental observation. The analysis was based on the assumption, the effluent is non-reacting, and the diffusion process is Markov process. In the photochemical smog, the above assumption may no longer be true. It is thus necessary to further work toward the solution of this more complicated problem.

VI. Proposed Work

With the present state of the model, there are some problems that must be considered. The work so far has concentrated on a simple puff of pollutants. There is no consideration of the interaction between two or more than two puffs. Strictly speaking, this is not what is occurring in reality.

As an individual puff travels and expands, there must be certain interaction between these puffs. Also the model is limited to the case when a puff is released into clean air. It is thus natural to consider the problem that a puff expands and takes up pollutants along the way as it travels into the atmosphere.

The derivation of ψ in Chapter V results in the form proposed by Gifford (1957), but experiments have shown that ψ in Gaussian form is not correct. The uncertainty in ψ is likely to be the results of the atmospheric dispersion, which is not a Markov process. Physical realities are more complicated than that assumed in Chapter V, for example, diffusion in the x, y and z direction was assumed to be independent.

Usually, some practical problems can be solved only by experimental methods. The dispersion of chemically reactive contaminants in the atmosphere over a complicated terrain is one which needs experimental study, possibly by wind-tunnel model experiments. However, a wind-tunnel model of smoke diffusion is by no means an established and reliable technique for application to atmospheric processes. On the other hand, the technique of numerical solution of the fundamental differential equation which describes the phenomena has made great progress recently (HINO, 1968). This technique may be considered a

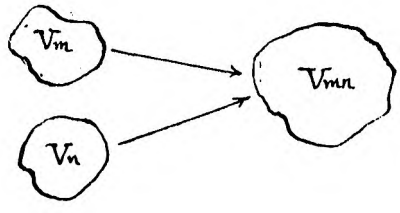
numerical experiment if we have full knowledge of the differential equations that describe the process. However, if the differential equations and appropriate boundary conditions do not fully describe the atmospheric processes, then the numerical experiment may be no better than an analogy to the wind-tunnel experiments.

Most of the liquid and solid particles in automobile emission are submicroscopic. One of the most serious aspects of photochemical smog is the generation and increasing concentration of these extremely small particles. These particles serve as condensation nuclei which may absorb pollutants. They may act as carriers for other pollutants and produce serious adverse effects to human beings.

In summary, I propose to investigate:

1. the effect of interaction between pollutant clouds from individual sources;
2. the probability density function ψ ;
3. the numerical solution of the Fickian diffusion equation with chemical reactions;
4. methods for the combination of the model for photochemical smog reactions developed in this report with the theories and experimental work on the particle size distribution;
5. a mathematical model of photochemical smog of Los Angeles basin (combining the results of (1)-(4) and using a more sophisticated chemical kinetic model, if available).

The starting point of (1) assumes each cloud is a variable volume continuously stirred tank reactor (VVCSTR). When two clouds meet together they are considered completely mixed and form another VVCSTR.



The mass balance for each VVCSTR is

$$V_m \frac{d}{dt}(C_j)_m = (q_f)_m [(C_{jf})_m - (C_j)_m] + V_m (R_j)_m$$

$$V_n \frac{d}{dt}(C_j)_n = (q_f)_n [(C_{jf})_n - (C_j)_n] + V_n (R_j)_n$$

$$V_{mn} \frac{d}{dt}(C_j)_{mn} = (q_f)_{mn} [(C_{jf})_{mn} - (C_j)_{mn}] + V_{mn} (R_j)_{mn}$$

where

V = VOLUME OF VVCSTR

C_j = CONCENTRATION OF CHEMICAL SPECIES j

C_{jf} = FEED CONCENTRATION OF CHEMICAL SPECIES j

R_j = CHEMICAL REACTION RATE OF CHEMICAL SPECIES j

q_f = FEED FLOW RATE

Subscript m, n, mn refer to reactor m, n, mn, respectively. One can expect that this kind of model can be extended to many interacting clouds.

The approach to problem (2) by using the fundamental theories of stochastic process are not very promising. A more practical approach would employ semiempirical forms of the spatial concentration distribution of the effluent downwind from a source. For example, the concentration of an inert material emitted at a rate Q from a continuous point source at a height h is given by (PANOFSKY, 1969):

$$c(x,y,z) = \frac{Q}{2\pi u \sigma_y \sigma_z} \exp\left\{ -\frac{y^2}{2\sigma_y^2} - \frac{(z+h)^2}{2\sigma_z^2} - \frac{(z-h)^2}{2\sigma_z^2} \right\}$$

The above expression has been used in atmospheric diffusion predictions by Gifford (1968).

The problem (3) can be approached in idealized cases so that the differential equations properly describe the phenomena. The solution of problem (3) will employ a numerical method.

There is now experimental evidence which indicates that high concentration of very small particles are formed in the Los Angeles atmosphere (personal communication between S. K. FRIEDLANDER and K. T. WHITBY). This conclusion is consistent with the experimental result of Lee and Patterson (1969), which indicates that the concentration of nitrates, formed as a result of atmospheric chemical reaction, is high in the small particle portion of the spectrum.

The first step of approaching problem (4) will be the determination of the rate of formation of these small particles. By assuming the rate of formation of aerosol by photochemical reaction is proportional to some function f,

then $$\frac{dN}{dt} = K f([RH], [SO_4^=], [SO_2^=], [NO_3^=], \cdots)$$

where $\frac{dN}{dt}$ is rate of formation of aerosols, f is a function of the concentrations of chemical species which involves the photochemical reactions and K is a constant to be determined from experimental results.

With a known example of the wind field and meteorological condition of Los Angeles basin and the combination of the results of the proposed research topics (1) - (4) one should be able to formulate a mathematical model of photochemical smog of Los Angeles basin. It will thus have application to such problems as determining the degree to which each source contributes to the over-all pollution problem, and forecasting air pollution levels.

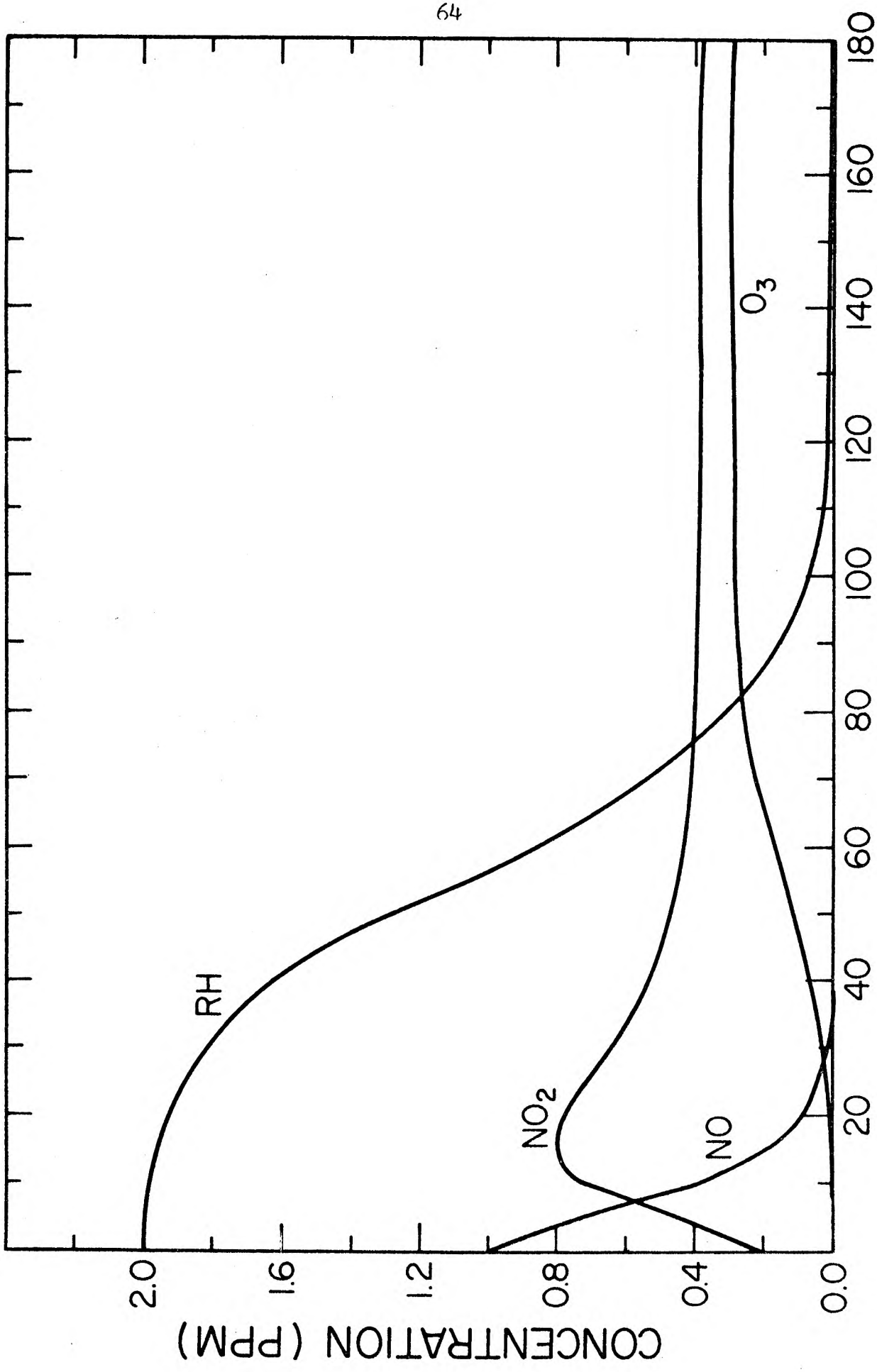

CONCENTRATION (PPM)
2.0
1.6
1.2
0.8
0.4
0.0
TIME (MIN)
20
40
60
80
100
120
140
160
180
RH
NO_2
NO
O_3

Figure 2

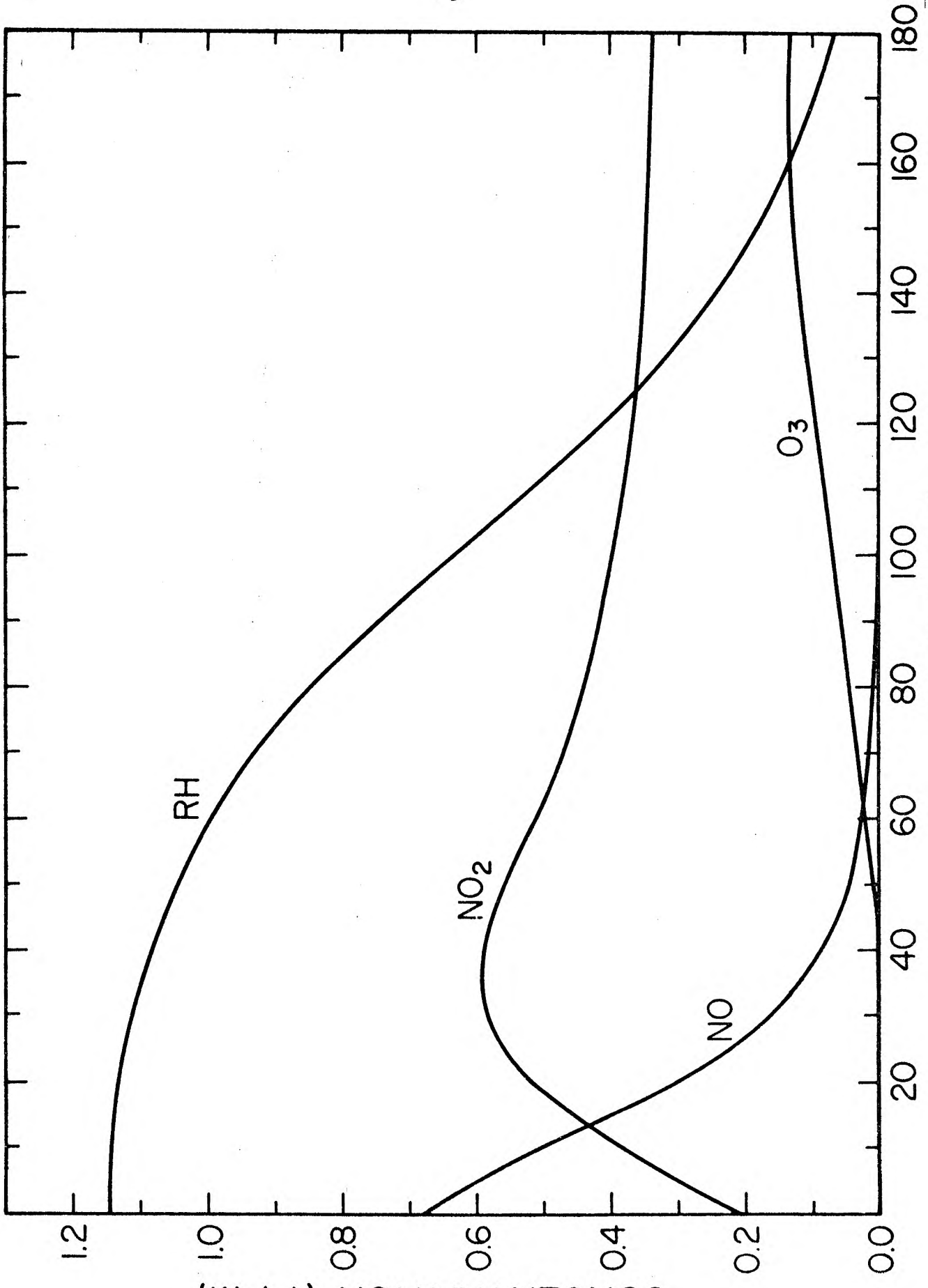

CONCENTRATION (PPM)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
TIME (MIN)
20
40
60
80
100
120
140
160
180
RH
NO_2
NO
O_3

Figure 3

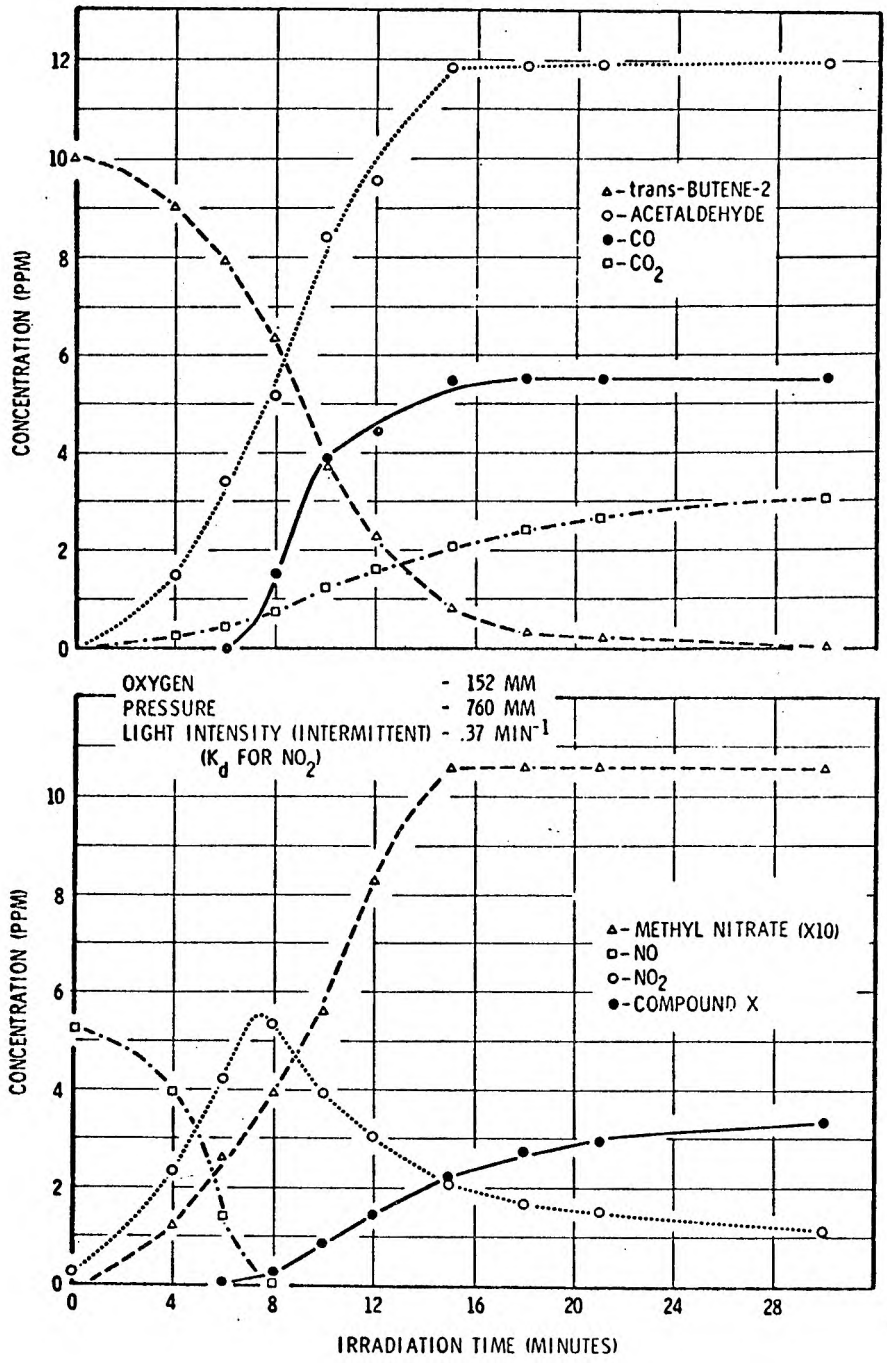


Figure 4 - Concentration Changes During Photooxidation. (TUESDAY, 1961)

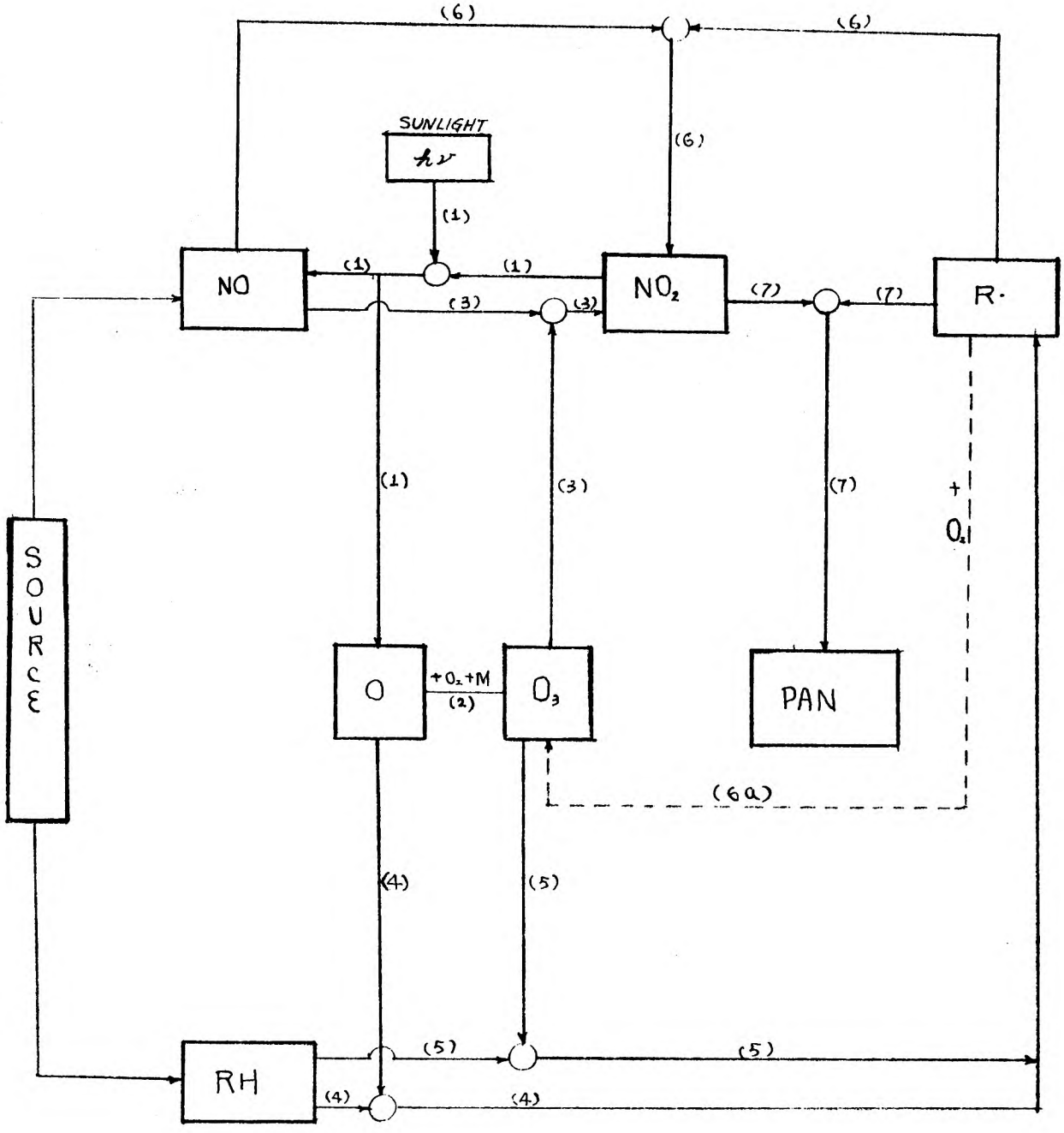


Fig. 5. Lumped-parameter reaction scheme
(number in parenthesis indicates reaction number)

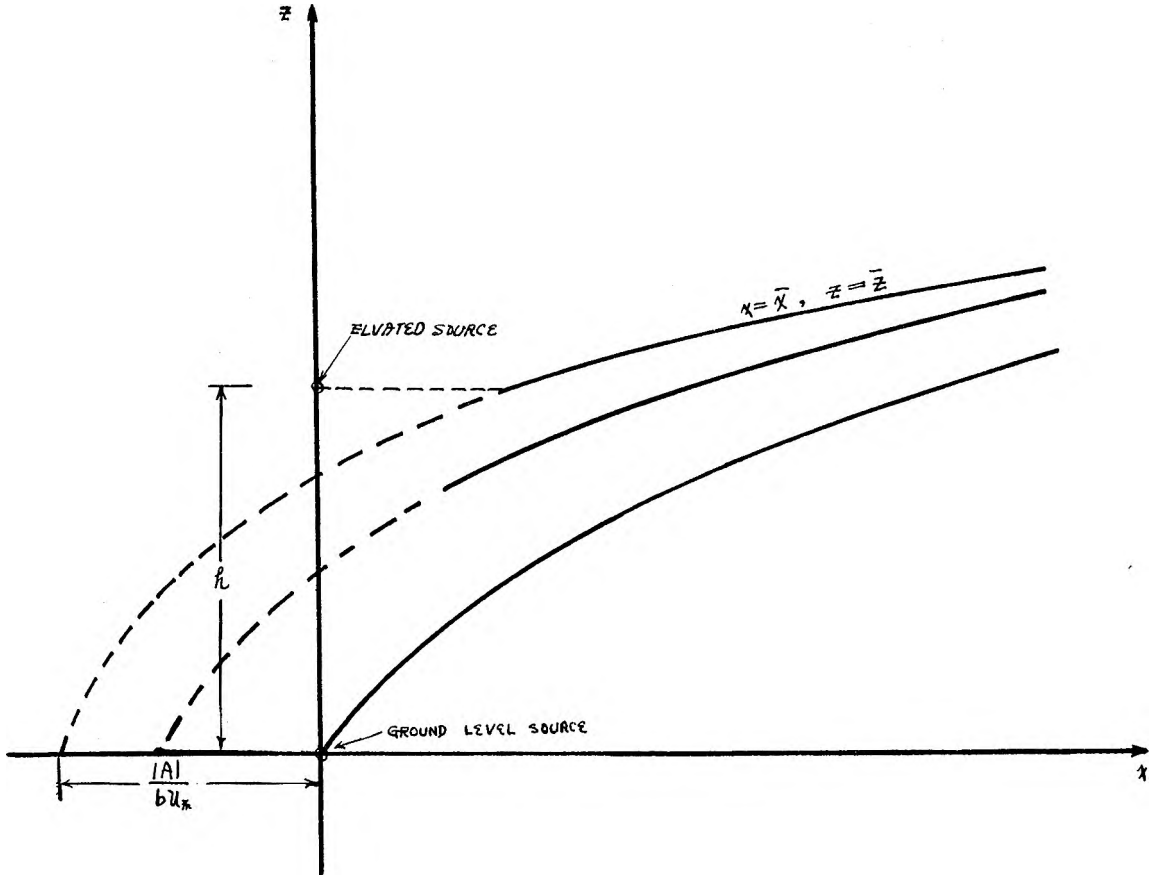


Fig. 6. Sketch of the path of a point which moves with the mean velocity of a particle released from a source (Batchelor, 1964)

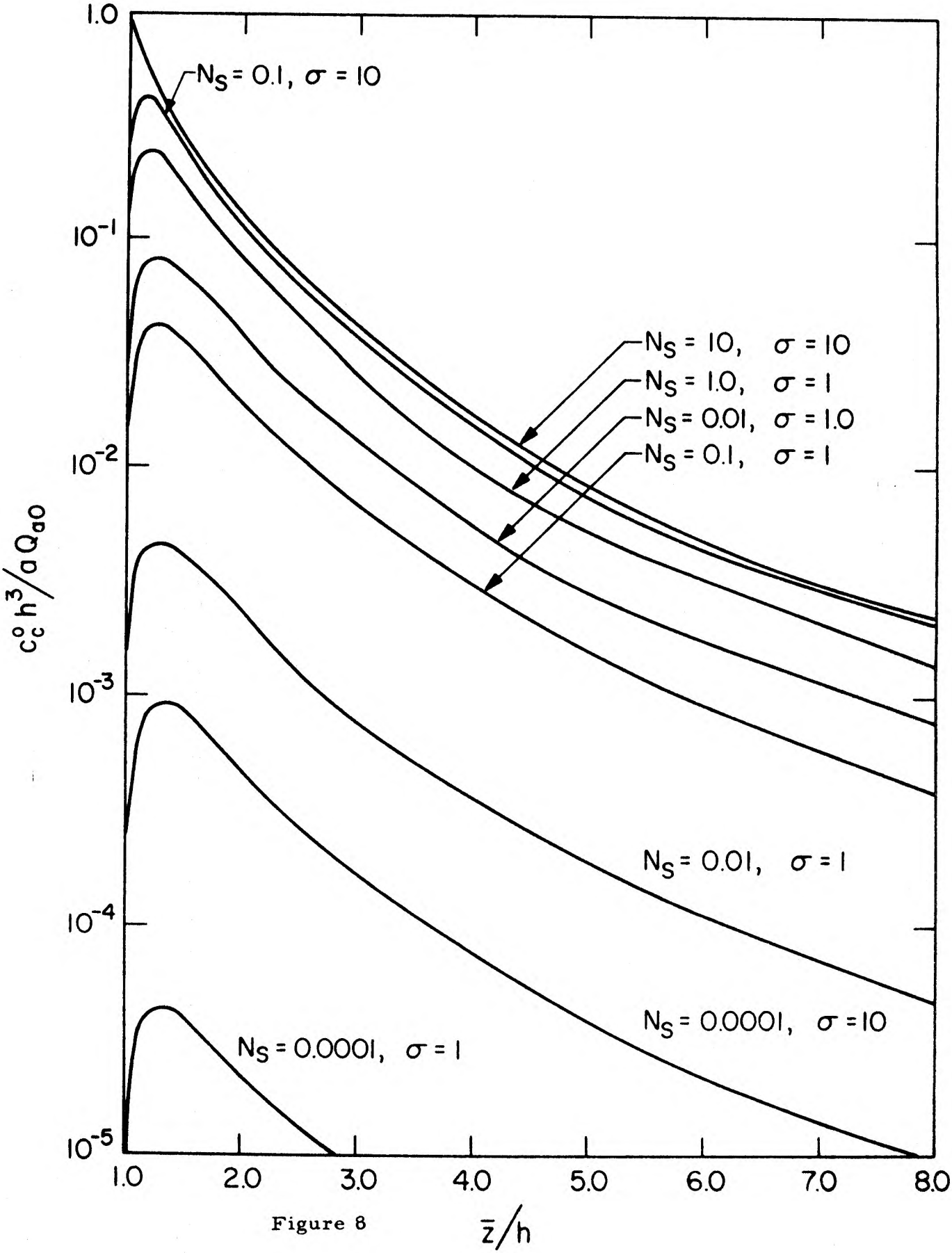

1.0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
$N_S = 0.1, \sigma = 10$
$N_S = 10, \sigma = 10$
$N_S = 1.0, \sigma = 1$
$N_S = 0.01, \sigma = 1.0$
$N_S = 0.1, \sigma = 1$
$N_S = 0.01, \sigma = 1$
$N_S = 0.0001, \sigma = 10$
$N_S = 0.0001, \sigma = 1$
$c_c^o h^3 / a Q_{a0}$
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
$\bar{z}/h$

Figure 8

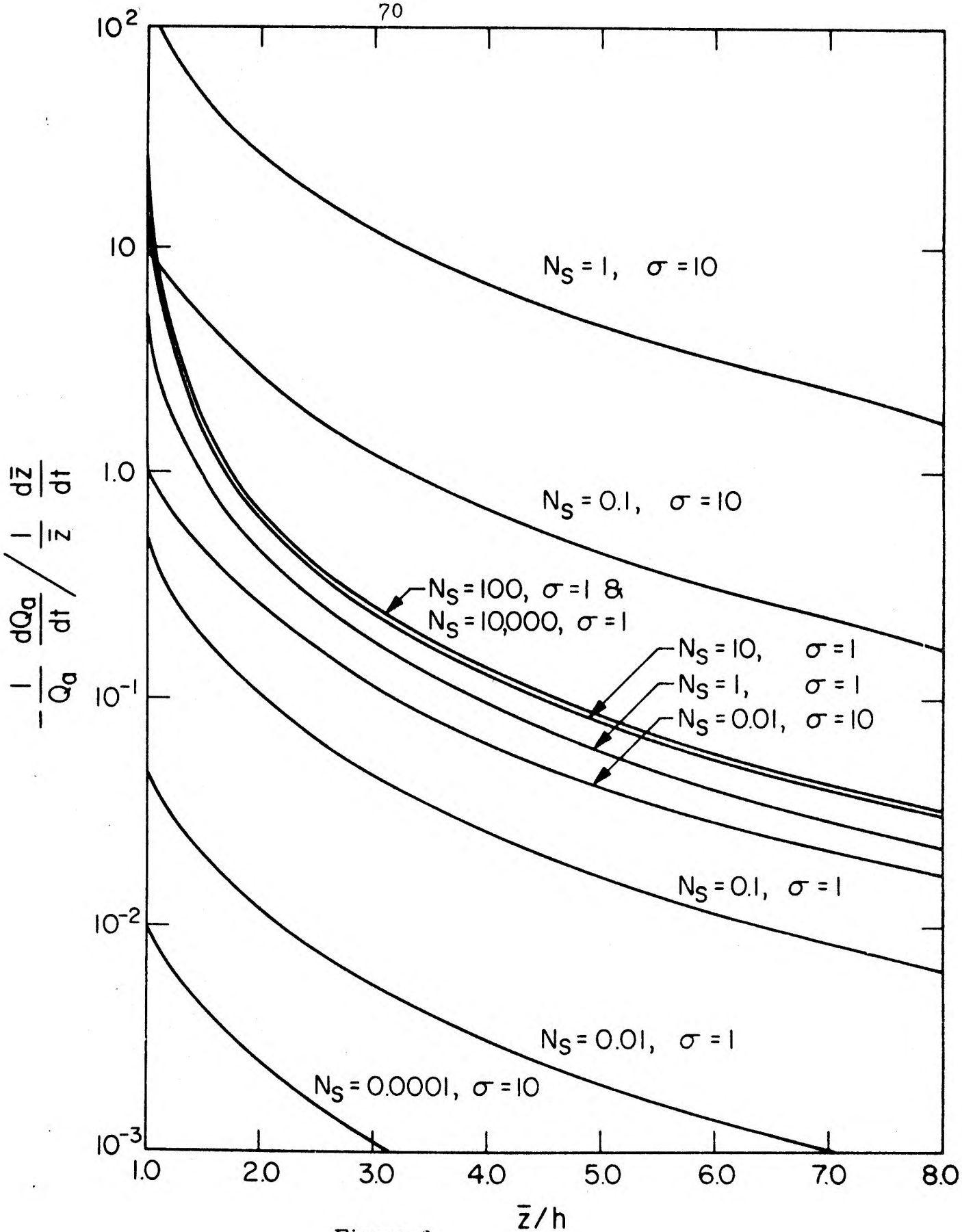

10^2
10
1.0
10^{-1}
10^{-2}
10^{-3}
$-\frac{1}{Q_a}\frac{dQ_a}{dt} \Big/ -\frac{1}{\bar{z}}\frac{d\bar{z}}{dt}$
$N_S = 1, \quad \sigma = 10$
$N_S = 0.1, \quad \sigma = 10$
$N_S = 100, \sigma = 1$ &
$N_S = 10{,}000, \sigma = 1$
$N_S = 10, \quad \sigma = 1$
$N_S = 1, \quad \sigma = 1$
$N_S = 0.01, \quad \sigma = 10$
$N_S = 0.1, \quad \sigma = 1$
$N_S = 0.01, \quad \sigma = 1$
$N_S = 0.0001, \sigma = 10$
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
$\bar{z}/h$

Figure 9

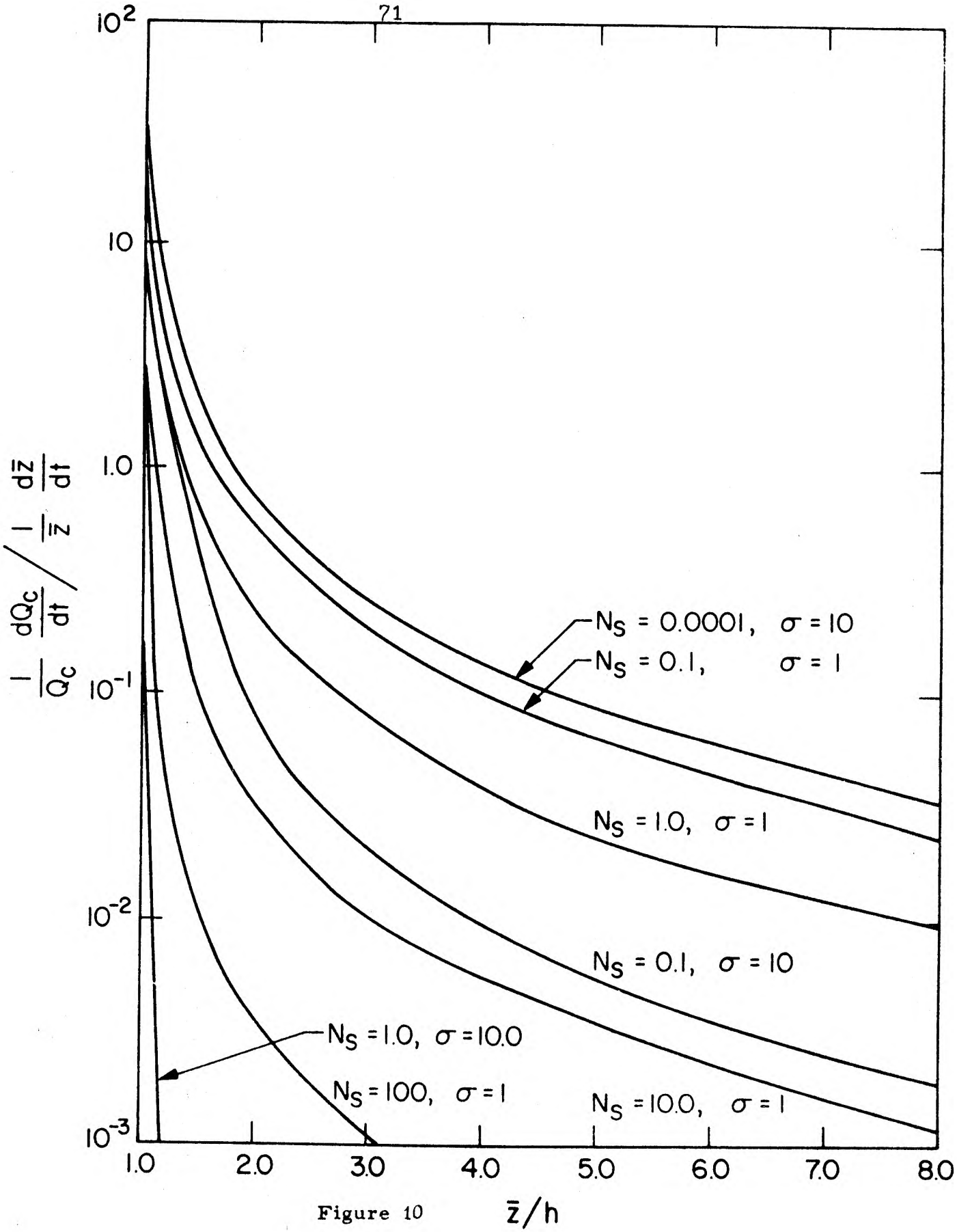

10^2
10
1.0
10^{-1}
10^{-2}
10^{-3}
$-\frac{1}{Q_c}\frac{dQ_c}{dt} \Big/ -\frac{1}{\bar{z}}\frac{d\bar{z}}{dt}$
$N_S = 0.0001, \quad \sigma = 10$
$N_S = 0.1, \quad \sigma = 1$
$N_S = 1.0, \quad \sigma = 1$
$N_S = 0.1, \quad \sigma = 10$
$N_S = 1.0, \quad \sigma = 10.0$
$N_S = 100, \quad \sigma = 1$
$N_S = 10.0, \quad \sigma = 1$
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
$\bar{z}/h$

Figure 10

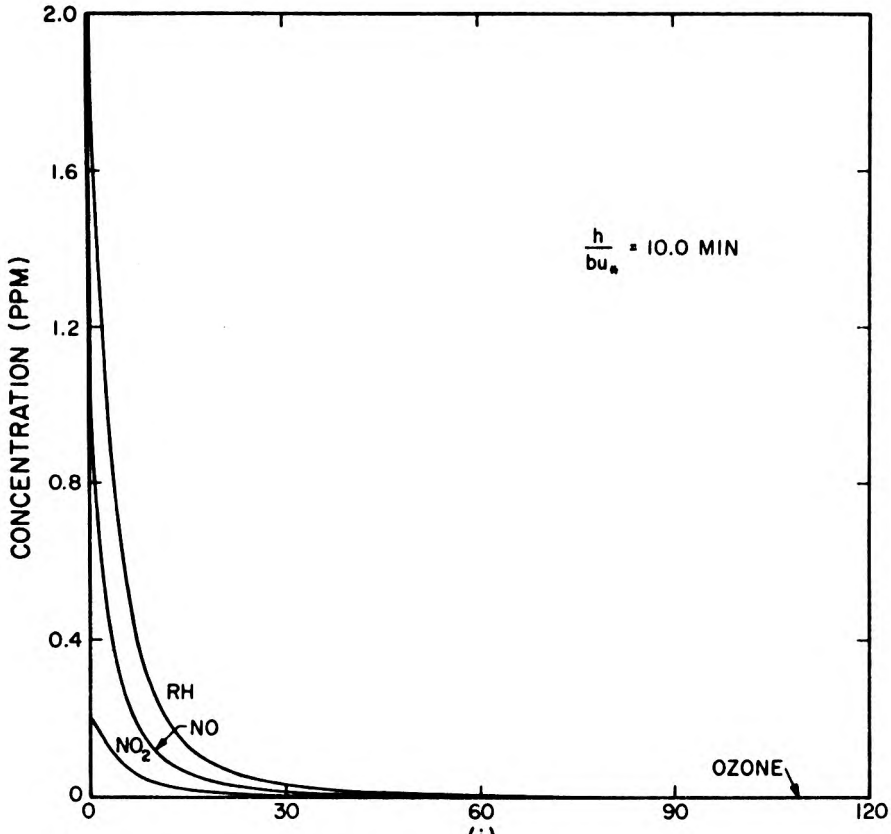

2.0
1.6
1.2
0.8
0.4
0
CONCENTRATION (PPM)
h/bu* = 10.0 MIN
RH
NO
NO2
OZONE
0
30
60
90
120
(i)

FIG. 11

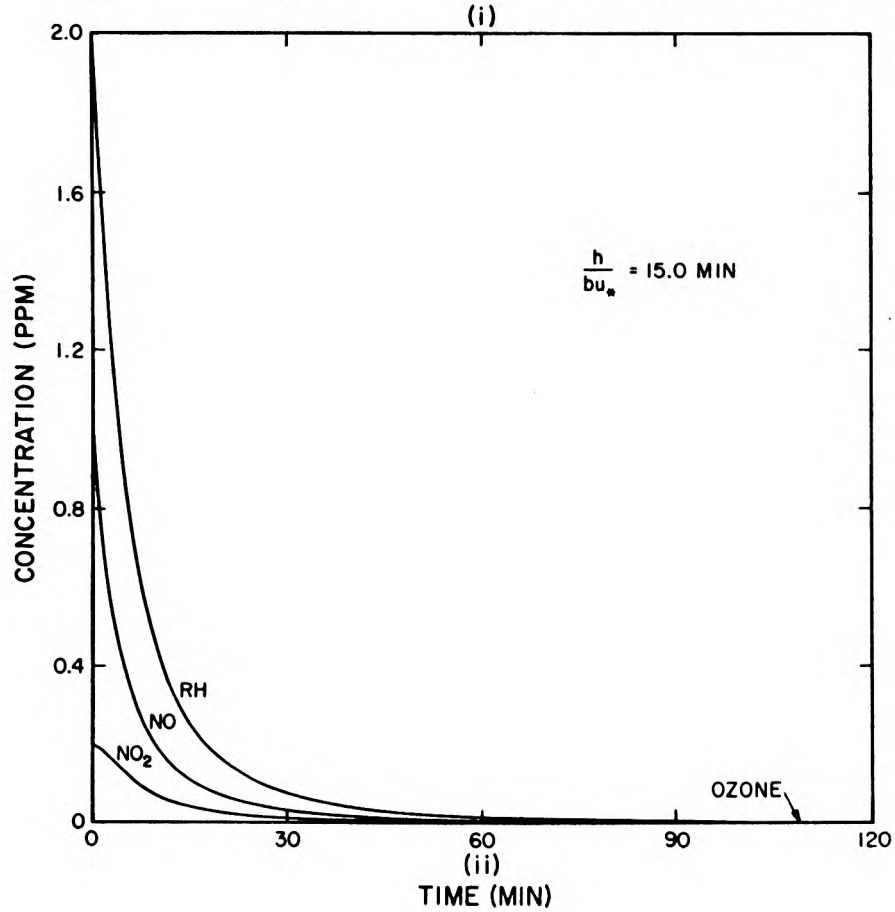

2.0
1.6
1.2
0.8
0.4
0
CONCENTRATION (PPM)
h/bu* = 15.0 MIN
RH
NO
NO2
OZONE
0
30
60
90
120
(ii)
TIME (MIN)

FIG. 12

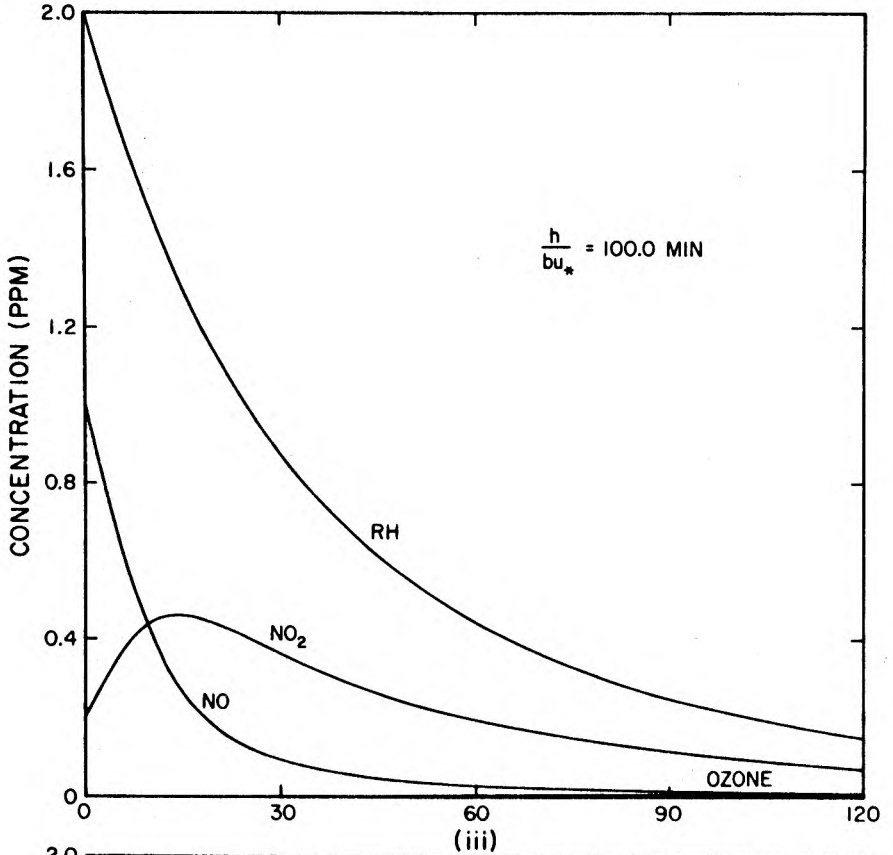

2.0
1.6
1.2
0.8
0.4
0
CONCENTRATION (PPM)
h/bu* = 100.0 MIN
RH
NO2
NO
OZONE
0
30
60
90
120
(iii)

FIG. 13

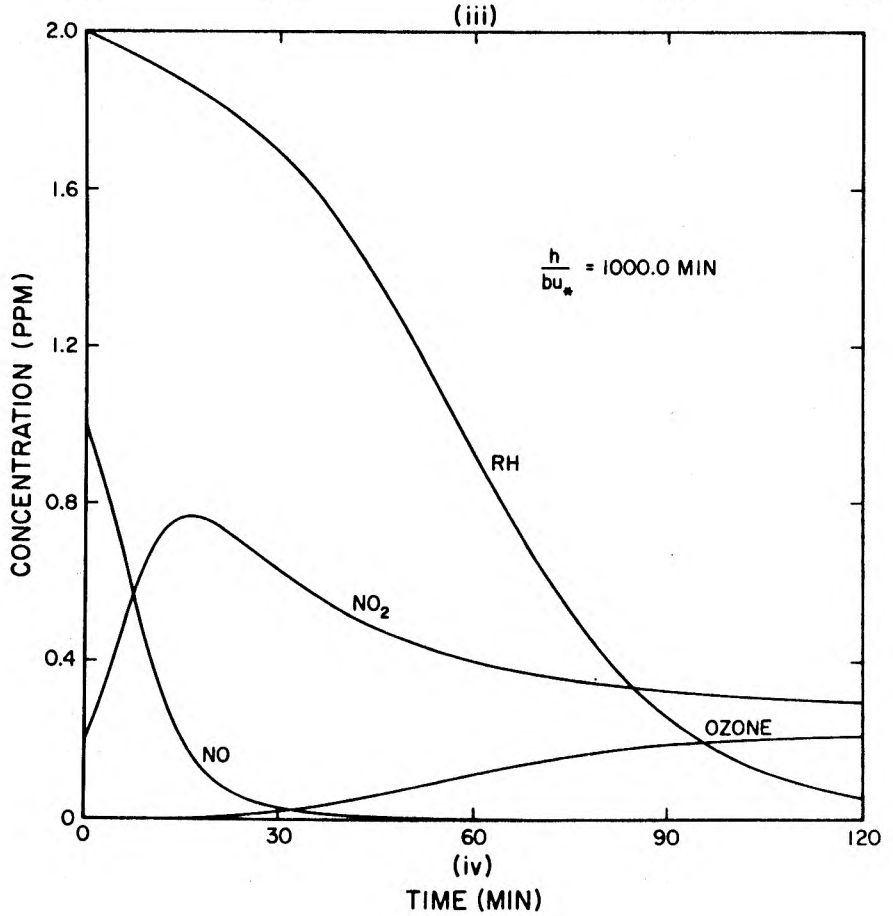

2.0
1.6
1.2
0.8
0.4
0
CONCENTRATION (PPM)
h/bu* = 1000.0 MIN
RH
NO2
NO
OZONE
0
30
60
90
120
(iv)
TIME (MIN)

FIG. 14

TABLE I.

Motor Vehicle Emission Standards,
California State Department of Public Health

Source	Engine size (cube-inch displacement)	Standards
Exhaust hydrocarbons	<50	---
	50-100	410 ppm by volume
	101-140	350
	>140	275
Exhaust carbon monoxide	<50	---
	50-100	2.3%
	101-140	2.0%
	> 140	1.5%
Exhaust oxides of nitrogen	All vehicles	350 ppm by volume
Crank case emission	All vehicles	0.1% supplied fuel
Carburetor emission	All vehicles	2 grams per soak
Fuel-tank emission	All vehicles	6 grams per day

TABLE II.

Comparison of the Reaction Rate Constants of the Ultrasimplified Model and the Compact Chemical Reaction Scheme

	Ultrasimplified Model	Compact Chemical Reaction Scheme, RH = C_4H_8
α	0.1 $ppm^{-2}min^{-1}$	0.145
λ	0.02 $ppm^{-2}min^{-1}$	0.0184
θ	$1.83 \times 10^{-3} ppm^{-1}min^{-1}$	1.5×10^{-4}
μ	$2.45 \times 10^{-4} min^{-1}$	1.98×10^{-3}

TABLE III.

DATA ON DIFFUSION IN NEUTRAL CONDITION

Continuous Point Sources		
Experiment	x (ft)	m in $c \propto x^m$
Davar 1961	1.5	-1.20
	4.5	-1.47
Malhotra 1962	4.5	-1.47
Wieghardt 1948	1.03	-1.42
Porton (Pasquil, 1962)	1640	-1.76
Prairie Grass (Cramer 1957)	1976	-1.8

Continuous Line Source		
Porton (Pasquil, 1962)	1640	-0.9-1.0
Malhotra 1962	4.5	- 0.8
Poreh 1962	7.5	- 0.9
Wieghardt	1.23	- 0.9

Nomenclature

Roman Letters

A_j	dimensionless constant defined in Eq. 76
B_j	defined in Eq. 87
a	dimensionless constant defined in Eq. 77
b	universal constant defined in Eq. 35
C	a constant defined in Eq. 38
c_i	instantaneous concentration of species i
$\overline{c_i}$	average concentration of species i
c_i'	fluctuating concentration of species i
C_p	specific heat at constant pressure
D_i	molecular diffusivity for species i
$\vec{F}(\eta_x, \eta_y, \eta_z)$	dimensionless velocity defined in Eq. 64
$f_i(\eta_x, \eta_y, \eta_z, t)$	dimensionless reaction rate defined in Eq. 63
$\vec{G}(\eta_x, \eta_y, \eta_z)$	dimensionless function defined in Eq. 65
H	inversion height
h	source height
k	von Karman constant
K_j $(j = x, y, z)$	eddy diffusivities of material defined in Eq. 4
k_i	reaction rate constant
L	Monin-Obukhov length defined in Eq. 28
l	Pranetl's mixing length
M	third body
N_s	dimensionless group defined in Eq. 110
n	number of chemical species
n_i	effective concentration of component i , defined in Eq. 118

Roman Letters

Q_i	moles of species i in cloud
q	heat flux in z-direction
r_i	reaction rate of species i
$\bar{r}_i$	average reaction rate of species i
S	effective area covered by the cloud
t	time
T	average absolute temperature
$V_i(x)$	mass of species i crossing the plane at x
$\vec{v}$	wind velocity vector
$\vec{v}'$	fluctuating velocity vector
u_*	friction velocity
$\vec{u}_R$	velocity vector relative to cloud center
$W_i(x)$	mass of species i per unit time crossing plane at x
x, y, z	coordinate position in atmospheric surface layer
$\bar{x}, \bar{y}, \bar{z}$	coordinate of the average position of the particle in the atmospheric surface layer

Greek Letters

α	parameter defined in Eq. 16
α_{ij}	order of reaction of species j in i th chemical reaction
ϵ	number of radicals generated per radical consumed
ζ	$\bar{z}/L$
η_x, η_y, η_z	dimensionless coordinates defined in Eq. 59
θ	parameter defined in Eq. 18
Λ	defined in Eq. 84
λ	parameter defined in Eq. 17
μ	parameter defined in Eq. 19
ρ	air density

σ	Q_{Bo}/Q_{Ao}
τ	characteristic time
τ_o	shearing stress at wall
ϕ	universal function defined in Eq. (28a)
Φ	quantum yield
ψ	probability density function

Superscript

-	average value
o	ground level concentration

Subscript

cls	continuous line source
cps	continuous point source
ips	instantaneous point source

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PROPOSITION

The Self-Preserving Particle Size Distribution for Coagulation by Brownian Motion--

Smoluchowski Coagulation and Simultaneous Maxwellian Condensation

ABSTRACT

A theoretical study has been made of the dynamics of coagulation with simultaneous condensation and of the behavior of the particle size distribution function. For coagulation and condensation in the continuum region the existence of self-preserving spectra--as defined in the papers of Friedlander and Wang (1966), Wang and Friedlander (1967)--depends on a nondimensional parameter $C = \frac{3\mu}{4kT} \cdot \frac{2B(S-1)}{\phi^{\frac{2}{3}} N^{\frac{1}{3}}}$ where μ and T are viscosity and temperature of the medium, k is the Boltzmann's constant, ϕ the total volume concentration, N the total number concentration of particles, B the proportionality coefficient in the equation for condensation rate and S the saturation ratio. For $C = 0$ phase equilibrium exists while for $C > 0$ simultaneous condensation and coagulation occur. For $C = 1.09$ the total surface concentration (surface area of particles per unit volume of gas) is invariant with respect to time. For other values of C saturation ratio must vary with time in a particular way in order for the system to be self-preserving. The shape of the self-preserving spectra are strongly dependent on C. Analytical solutions of the transformed kinetic equation have been found for the lower and upper end of the spectrum and numerical solutions for the entire spectrum have been calculated for four values of C. The theory is limited to values of C smaller than of order unity. Good agreement with experiments is found applying developed theory to the calculation of the polydispersity factor.

I. EQUATION OF COAGULATION AND CONDENSATION

The existing theory of self-preserving size spectra as developed in the previous two papers by FRIEDLANDER and WANG (1966, 1967) does not take into account vapor condensation on the particles, a process which frequently occurs in aerosol systems. The basic kinetic equation describing simultaneous coagulation and condensation in a homogeneous system (particle concentration independent of position) can be written as follows LEVIN and SEDUNOV (1967):

$$\frac{\partial n(v,t)}{\partial t} + \frac{\partial}{\partial v}\left\{I(v,t)\, n(v,t)\right\} = \frac{1}{2}\int_0^v \beta(\tilde{v},\, v-\tilde{v})\, n(\tilde{v},t)\, n(v-\tilde{v})\, d\tilde{v} - \int_0^\infty \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v},t)\, d\tilde{v} \qquad (1)$$

where $n(v,t)$ is the particle volume distribution function, v the particle volume, t the time, $I(v,t) = \frac{dv}{dt}$ the rate of condensation and $\beta(v,\tilde{v})$ the collision parameter (also referred to as collision frequency factor or coagulation constant) for particles of volumes v and $\tilde{v}$. In this formulation, particles are neither lost nor gained by evaporation or condensation which means, for example, that homogeneous nucleation is not taking place in the case of condensation. A justification for this assumption is given later. For $I(v,t) = 0$ equation (1) reduces to the well-known Smoluchowski equation describing coagulation in a polydisperse system. The physical interpretation of the terms on the right side of equation (1) has been given by a number of authors (HIDY and BROCK, 1970; HULBURT and KATZ, 1964; ZEBEL , 1966).

Two important moments of $n(v,t)$ are the total number of concentration $N(t)$ given by

$$N(t) = \int_0^\infty n(v,t)\,dv \tag{2}$$

and the total volume concentration $\phi_{(t)}$ given by

$$\phi(t) = \int_0^\infty v\, n(v,t)\,dv \tag{3}$$

Integrating equation (1) with respect to v from 0 to ∞ gives (see Appendix I)

$$\frac{dN}{dt} = -\frac{1}{2}\int_0^\infty\int_0^\infty \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v},t)\,d\tilde{v}\,dv \tag{4}$$

Defining the collision parameter of a polydisperse system by

$$A_0 = \frac{1}{2}\int_0^\infty\int_0^\infty \beta(v,\tilde{v})\, f_v(v,t)\, f_v(\tilde{v},t)\,d\tilde{v}\,dv = \frac{1}{2N^2}\int_0^\infty\int_0^\infty \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v},t)\,d\tilde{v}\,dv \tag{5}$$

where $f_v(v,t) = \dfrac{n(v,t)}{N(t)}$ is the normalized volume distribution function, equation (4) becomes

$$\frac{dN}{dt} = -A_0 N^2 \tag{6}$$

Similarly, multiplying (1) by v and integrating with respect to v from 0 to ∞ gives (see Appendix II)

$$\frac{d\phi}{dt} = \int_0^\infty I(v,t)\, n(v,t)\,dv \tag{7}$$

From (7) it follows that if $I(v;t) = 0$, $\emptyset$ is invariant with respect to time.

The case of Smoluchowski coagulation, that is, diffusion controlled coagulation of particles much larger than the mean free path of the gas molecules is a classical problem in coagulation theory with many important applications. The particles are assumed to be spherical and electrically neutral. The collision parameter $\beta(v, \tilde{v})$ is given by SMOLUCHOWSKI (1916)

$$\beta(v, \tilde{v}) = \frac{2kT}{3\mu}\left(v^{\frac{1}{3}} + \tilde{v}^{\frac{1}{3}}\right)\left(v^{-\frac{1}{3}} + \tilde{v}^{-\frac{1}{3}}\right) \tag{8}$$

is a homogeneous function of zero order consistent with the requirement for self-preserving spectra discussed in papers by FRIEDLANDER and WANG (1967). The rate of condensation for negligibly small Knudsen numbers is given by the Maxwell equation (FUCHS , 1959) which, if the effects of latent heat are taken into account (see Appendix III), becomes

$$I(v,t) = \frac{dv}{dt} = \mathcal{B}(S-1)\, v^{\frac{1}{3}}$$

where

$$\mathcal{B} = 3^{\frac{1}{3}}(4\pi)^{\frac{2}{3}}\left\{\frac{\rho L^2 M}{\chi R T^2} + \frac{\rho R T}{D M p_s}\right\}^{-1} \tag{9}$$

and $S = \frac{p_v}{p_s}$ is the saturation ratio, p_v the actual pressure of the vapor, p_s the saturation vapor pressure, L the latent heat, M the molecular weight of the vapor, ρ the density of the liquid, χ the thermal conductivity of the medium, T the absolute temperature of the medium, R the gas constant and D the diffusion coefficient of the vapor. The condensation rate is implicitly a function of time because the saturation ratio may vary with time.

We now introduce the similarity transformation of FRIEDLANDER (1960a, 1960b, 1961, 1962) and SWIFT and FRIEDLANDER (1964):

$$n(v,t) = \frac{N^2(t)}{\phi(t)}\psi(\eta) \quad ; \quad \eta = \frac{N(t)\,v}{\phi(t)} \tag{10}$$

Unlike the problems treated in the previous papers by FRIEDLANDER and WANG (1966, 1967), volume concentration ϕ is a function of time as a result of the condensation process.

Since $v^* = \phi/N$ is a mean particle volume, the new independent variable η can be written $\eta = v/v^*$ and $\psi(\eta)$ can be interpreted as a dimensionless distribution function. It is called "self-preserving" since its shape does not change with time when $\psi(\eta)$ is represented as a function of η. It can be shown (FRIEDLANDER and WANG, 1966) in certain cases that the self-preserving distribution is the asymptotic distribution attained in a coagulating system after a sufficiently long time. The numerical experiments of HIDY (1965) also support this hypothesis. A general proof does not exist however.

Substitution equation (10) in equation (1) with equations (8) and (9) for $\beta(v,\tilde{v})$ and $I(v,t)$, the result after some manipulation is:

$$(1+\mu_1\mu_3)\left\{2\psi(\eta)+\eta\frac{d\psi}{d\eta}\right\}+\int_0^{\eta}\left\{1+(\eta-\tilde{\eta})^{\frac{1}{3}}\tilde{\eta}^{-\frac{1}{3}}\right\}\psi(\tilde{\eta})\,\psi(\eta-\tilde{\eta})\,d\tilde{\eta}+$$
$$-\psi(\eta)\left\{2+\mu_3\eta^{-\frac{1}{3}}+\mu_1\eta^{\frac{1}{3}}\right\}+\frac{3\mu}{4\kappa T}\cdot\frac{2}{\phi^{\frac{2}{3}}N^{\frac{1}{3}}}B(S-1)\left\{\mu_3\psi(\eta)+\mu_3\eta\frac{d\psi}{d\eta}+\right.$$
$$\left.-\eta^{\frac{1}{3}}\frac{d\psi}{d\eta}-\frac{1}{3}\eta^{-\frac{2}{3}}\psi(\eta)\right\}=0 \tag{11}$$

where

$$\mu_1=\int_0^{\infty}\eta^{-\frac{1}{3}}\psi(\eta)\,d\eta$$

and

$$\mu_3 = \int_0^\infty \eta^{\frac{1}{3}} \psi(\eta) d\eta$$

An equivalent expression was first given by WANG (1966).

II. CRITERIA FOR SELF-PRESERVING SPECTRA

When the dimensionless group

$$C = \frac{3\mu}{4kT} \cdot \frac{2}{\phi^{\frac{2}{3}} N^{\frac{1}{3}}} \cdot B(S-1) \tag{12}$$

is constant, equation (11) is an ordinary integro-differential equation consistent with the original assumption that ψ is a function only of η . The dimensionless group C which appears in (11) can be rewritten as follows:

$$\frac{C}{1+\mu_1\mu_3} = \frac{\left(\frac{1}{v^+}\frac{dv^+}{dt}\right)_{COND.}}{\left(-\frac{1}{N}\frac{dN}{dt}\right)_{COAG}} = \frac{B(S-1)(v^+)^{\frac{2}{3}}}{\frac{2kT}{3\mu}(1+\mu_1\mu_3)N} \tag{13}$$

The numerator is the fractional rate of change in the volume of a particle of average size due to condensation. The denominator is the negative of the fractional rate of change in the number of particles resulting from coagulation. Hence, C can be interpreted as a measure of the relative rates of condensation and coagulation. When C is small, the condensation process proceeds slowly compared with the coagulation process. The variation with time of the total number, volume and surface concentrations can now be obtained. Using (8) and (10) equation (5) gives

$$A_0 = \frac{2kT}{3\mu}(1+\mu_1\mu_3) \tag{14}$$

Using (14) the solution of (6) becomes

$$N = \frac{N_0}{1+\frac{2kT}{3\mu}(1+\mu_1\mu_3)N_0 t} \tag{15}$$

where $N_o = N(0)$

From (7) using (9), (10) and (12)

$$\frac{d\phi}{dt} = \frac{2kT}{3\mu}\mu_3 C \phi N \tag{16}$$

Integration of (16) with the aid of (15) gives

$$\phi = \phi_o \left\{ 1 + \frac{2kT}{3\mu}(1+\mu_1\mu_3)N_o t \right\}^{\frac{1}{2}K} \tag{17}$$

where $\phi_o = \phi(0)$ and $K = \frac{2\mu_3 C}{1+\mu_1\mu_3}$

Inserting (15) and (17) into (12) and supposing constant temperature gives an expression for the time dependence of the saturation ratio during the condensation-coagulation process:

$$S = 1 + \frac{2kTCN_o^{\frac{1}{3}}\phi_o^{\frac{2}{3}}}{3\mu B} \left\{ 1 + \frac{2kT}{3\mu}(1+\mu_1\mu_3)N_o t \right\}^{\frac{1}{3}(K-1)} \tag{18}$$

The saturation ratio must vary in this way in order for self-preserving spectra to exist. The actual time dependence of the saturation ratio depends on the behavior of the sources and sinks of the saturated vapor to which the aerosol is exposed.

The total surface area of particles per unit volume or surface concentration $\sigma(t)$ is given by

$$\sigma(t) = (36\pi)^{\frac{1}{3}} \int_o^\infty v^{\frac{2}{3}} n(v,t)\, dv \tag{19}$$

Using (10) equation (19) becomes

$$\sigma = (36\pi)^{\frac{1}{3}} \mu_4 \phi^{\frac{2}{3}} N^{\frac{1}{3}} \tag{20}$$

where

$$\mu_a = \int_0^\infty \eta^{\frac{a}{3}} \psi(\eta) d\eta \tag{21}$$

Inserting (15) and (17) into (20) gives

$$\sigma = \sigma_0 \left\{ 1 + \frac{2kT}{3\mu} (1 + \mu_1\mu_3) N_0 t \right\}^{\frac{1}{3}(K-1)} \tag{22}$$

where $\sigma_0 = \sigma(0) = (36\pi)^{\frac{1}{3}} \mu_4 \phi_0^{\frac{2}{3}} N_0^{\frac{1}{3}}$ is the initial value of the total surface concentration.

The value of K is of great importance in determining the behavior of a coagulating system with simultaneous condensation. Four different cases can be distinguished:

(1) When K = 0, C = 0 and no condensation occurs since the system is in a state of phase equilibrium. By (17) $\phi = \phi_0$, by (18) S = 1 and by (22) σ decreases with time as expected in the case of the coagulation of liquid particles. Equation (11) reduces to the problem treated by FRIEDLANDER and WANG (1966).

(2) When K = 1, $C = \frac{1}{2\mu_3}(1 + \mu_1\mu_3)$ and (18) requires that the saturation ration be constant. If the temperature is constant all external parameters (T, S, μ) must be constant. By (17) ϕ must increase in the following way:

$$\phi = \phi_0 \left\{ 1 + \frac{2kT}{3\mu} (1 + \mu_1\mu_3) N_0 t \right\}^{\frac{1}{2}} \tag{23}$$

From (18) the condition of self-preserving spectra in the case of constant saturation ratio is

$$N_0^{\frac{1}{3}} \phi_0^{\frac{2}{3}} \frac{kT(1 + \mu_1\mu_3)}{3\mu B(S-1)\mu_3} = 1 \tag{24}$$

By (22) $\sigma = \sigma_0$ which means that the surface concentration is constant. The decrease of surface area due to coagulation is, in this case, balanced by the formation of the new surface due to vapor

condensation.

(3) For $0 < K < 1$, $0 < C < \frac{1}{2\mu_3}(1+\mu_1\mu_3)$ and from (18) $S > 1$ as expected for condensation. The volume concentration $\emptyset$ increases according to (17) and the saturation ratio S decreases according to (18) as would be expected for a closed system. By (22) the surface concentration σ decreases, indicating that in this case coagulation controls.

(4) For $K > 1$, $C > \frac{1}{2\mu_3}(1+\mu_1\mu_3)$ and $\emptyset$ increases according to (17). By (18) S must increase with time in this case in order for the system to be self-preserving. By (22) surface concentration is increasing with time, indicating that in this case condensation controls. Limitation on values of C will be discussed later.

III. RELATIONSHIPS AMONG THE MOMENTS

It is convenient to use the following notation for the moments of particle size distribution function

$$\mu_i = \int_0^\infty \eta^{\frac{1}{3}(i-2)} \psi(\eta) d\eta \qquad i = 1, 2, \cdots, 5 \tag{25}$$

Several useful relationships exist among the moments. For example

$$\mu_1 = \int_0^\infty \eta^{-\frac{1}{3}} \psi(\eta) d\eta = r_3 \int_0^\infty \frac{1}{r} f_r(r) dr = r_3 \cdot \overline{\left(\frac{1}{r}\right)} = \frac{r_3}{r_H} \tag{26}$$

where r is the radius of the particle, $f_r(r)$ the normalized number-distribution function, r_3 the cube mean radius and r_H the harmonic mean radius. Similarly

$$\mu_3 = \int_0^\infty \eta^{\frac{1}{3}} \psi(\eta) d\eta = \frac{1}{r_3} \int_0^\infty r f_r(r) dr = \frac{r_1}{r_3} \tag{27}$$

where r_1 is the arithmetic mean radius, and

$$\mu_4 = \int_0^\infty \eta^{\frac{2}{3}} \psi(\eta) d\eta = \left(\frac{r_2}{r_3}\right)^2 \tag{28}$$

where $r_2^2 = \int_0^\infty r^2 f_r(r) dr$ is the mean square radius. According to HERDAN (1960)

$$r_H \leqq r_1 \leqq r_2 \leqq r_3 \tag{29}$$

Using (29) it can be concluded that

$$\mu_1 \geq 1 \quad , \quad 0 < \mu_3 \leq 1 \quad , \quad 0 < \mu_4 \leq 1 \quad , \quad \mu_1 \mu_3 \geq 1 \tag{30}$$

For a monodisperse system all mean radii are equal ($r_1 = r_2 = r_3 = r_H$) and $\mu_1 = \mu_3 = \mu_4 = 1$. Thus the deviations of μ_1, μ_3 and μ_4 from

unity can serve as a measure of the polydispersity of the system. This result will be used later. Substitution of (10) into equations (2) and (3) gives

$$\mu_2 = \int_0^\infty \psi(\eta) d\eta = 1 \tag{31}$$

and

$$\mu_5 = \int_0^\infty \eta^2 \psi(\eta) d\eta = 1 \tag{32}$$

Using (26) and (27) equation (14) becomes

$$A_0 = \frac{2kT}{3\mu}\left(1 + \frac{r_1}{r_H}\right) \tag{33}$$

From (33) it follows that a knowledge of r_1 and r_H or r_1 and $\left(\overline{\frac{1}{r}}\right)$ is sufficient for the determination of the collision parameter for a polydisperse system and the knowledge of the whole spectrum is not required. This statement for a self-preserving system in the continuum region is equivalent to the conclusion of TIKHOMIROV et al (1942). For a monodisperse system equation (33) or (14) gives, of course,

$$A_0 = \frac{4kT}{3\mu}$$

IV. ANALYTICAL SOLUTIONS OF THE TRANSFORMED KINETIC EQUATION

Equation (11) can also be written as follows

$$\int_0^{\eta} \left\{ 1 + (\eta-\tilde{\eta})^{\frac{1}{3}} \tilde{\eta}^{-\frac{1}{3}} \right\} \psi(\tilde{\eta})\, \psi(\eta-\tilde{\eta})\, d\tilde{\eta} + (\eta + \mu_1\mu_3 + \mu_3 C\eta - C\eta^{\frac{1}{3}}) \frac{d\psi}{d\eta} +$$

$$+ \left\{ 2\mu_1\mu_3 - \mu_3 \eta^{-\frac{1}{3}} - \mu_1 \eta^{\frac{1}{3}} + \mu_3 C - \frac{1}{3} C \eta^{-\frac{2}{3}} \right\} \psi(\eta) = 0 \qquad (34)$$

It does not seem possible to obtain a general analytical solution of this equation, although solutions for the lower and the upper end of the spectrum can be found using a modified version of the method of FRIEDLANDER and WANG (1966). It is assumed first that for sufficiently small values of η the integral term in (34) can be neglected. The solution of the resulting ordinary differential equation is given by

$$\psi(\eta) = C_1 \frac{(\eta^{\frac{1}{3}} - \eta_1^{\frac{1}{3}})^{\varepsilon-\omega}}{\eta^{\frac{1}{3}} (\eta^{\frac{1}{3}} + \eta_1^{\frac{1}{3}})^{\varepsilon+\omega}} \exp\left(\frac{3\mu_1}{1 + \mu_1\mu_3 + \mu_3 C} \eta^{\frac{1}{3}} \right) \qquad (35)$$

where

$$\eta_1 = \left\{ \frac{C}{1 + \mu_1\mu_3 + \mu_3 C} \right\}^{\frac{3}{2}}$$

C_1 is an integration constant and exponents ε and ω are given by

$$\varepsilon = \frac{3\mu_3}{2\sqrt{C}} (1 + \mu_1\mu_3 + \mu_3 C)^{-\frac{1}{2}} + \frac{3}{2} \mu_1 \sqrt{C}\, (1 + \mu_1\mu_3 + \mu_3 C)^{-\frac{3}{2}}$$

and

$$\omega = -\frac{1}{2} + (3\mu_1\mu_3 + \frac{3}{2}\mu_3 C)(1 + \mu_1\mu_3 + \mu_3 C)^{-1}$$

For $\eta < \eta_1$, Eq. (35) can no longer be applied. Instead, the solution of Eq. (34) is given by

$$\psi(\eta) = C_1' \frac{(\eta_1^{\frac{1}{3}} - \eta^{\frac{1}{3}})^{2-\omega}}{\eta^{\frac{1}{3}}(\eta_1^{\frac{1}{3}} + \eta^{\frac{1}{3}})^{2+\omega}} \exp\left(\frac{3\mu_1}{1+\mu_1\mu_3} \eta^{\frac{1}{3}} - \frac{\mu_3 C}{1+\mu_1\mu_3} \eta\right) \tag{35a}$$

where C_1' is another constant different from C_1. The boundary condition $\psi(\eta)=0$ at $\eta=0$ requires that $C_1' = 0$, so $\psi(\eta) = 0$ for $\eta < \eta_1$. This means that the integral term in (34) is identically zero over the range $\eta_1 < \eta < 2\eta_1$ so that (35) represents an exact solution to (34) over that range.

For C = 0 (35) reduces to

$$\psi(\eta) = C_1 \eta^{-\frac{2\mu_1\mu_3}{1+\mu_1\mu_3}} \exp\left(\frac{3\mu_1 \eta^{\frac{1}{3}} - 3\mu_3 \eta^{-\frac{1}{3}}}{1+\mu_1\mu_3}\right) \tag{36}$$

which is the solution of FRIEDLANDER and WANG (1966) for Smoluchowski coagulation. For the upper end of the spectrum, that is for $\eta \longrightarrow \infty$ equation (34) reduces to

$$\int_0^\eta \left\{1 + (\eta - \hat{\eta})^{\frac{1}{3}} \hat{\eta}^{-\frac{1}{3}}\right\} \psi(\hat{\eta}) \psi(\eta - \hat{\eta}) d\hat{\eta} + \left\{\eta + \mu_1\mu_3\eta + \mu_3 C\eta\right\} \frac{d\psi}{d\eta} = 0 \tag{37}$$

A solution of this equation is

$$\psi(\eta) = C_2 \frac{1 + \mu_1\mu_3 + \mu_3 C}{1 + \Gamma(\frac{2}{3})\Gamma(\frac{4}{3})} \exp(-C_2\eta) \tag{38}$$

where C_2 is an integration constant and Γ is the gamma function.

The approximations in this derivation are discussed by FRIEDLANDER and WANG (1966) in their treatment of the upper end of the spectrum.

V. NUMERICAL SOLUTIONS OF THE TRANSFORMED KINETIC EQUATION

Equation (34) is a nonlinear ordinary integro-differential equation for $\Psi(\eta)$ which must be solved with certain constraints on the moments of $\Psi(\eta)$, given by equations (26), (27), (31) and (32).

For the case of C = 0 FRIEDLANDER and WANG (1966) reduced the two undetermined constants μ_1 and μ_3 to one by an appropriate transformation. For $C \neq 0$ this transformation is no longer applicable and a trial-and-error procedure becomes necessary. Among the approximate methods which exist at present the finite difference method is probably the most accurate. The Adams extrapolation formula (COLLATZ, 1960) truncated after the fourth difference term was used. The starting values for the Adams extrapolation were calculated using the analytical solution for the lower end of the spectrum (35).

To facilitate numerical computation equation (34) was transformed using the substitution $\eta = e^{x}$ and $\Psi(\eta) = Y(x)$. The result is

$$\left(1 + \mu_1\mu_3 + \mu_3 C - C e^{-\frac{2}{3}x}\right)\frac{dY}{dx} = -\left\{2\mu_1\mu_3 + \mu_3 C - \mu_3 e^{-\frac{1}{3}x} - \mu_1 e^{\frac{1}{3}x} - \frac{1}{3} C e^{-\frac{2}{3}x}\right\} x$$

$$\times Y(x) - \int_{-\infty}^{x} \left\{1 + (e^{x} - e^{\hat{x}})^{\frac{1}{3}} e^{-\frac{1}{3}\hat{x}}\right\} Y(\hat{x})\, Y(\ln(e^{x} - e^{\hat{x}}))\, e^{\hat{x}}\, d\hat{x} \qquad (39)$$

The integral term in (39) was further transformed into the form

$$\frac{3}{2} e^{x} \int_{0}^{\infty} \left\{e^{-\frac{1}{2}z} + (1 - e^{-\frac{3}{2}z})^{\frac{1}{3}}\right\} Y(x - \tfrac{3}{2}z)\, Y\left[x + \ln(1 - e^{-\frac{3}{2}z})\right] e^{-z}\, dz$$

by the substitution $z = \frac{2}{3}(x - \hat{x})$. The value of the integral was computed by the 32-point Gaussian-Laguerre quadrature formula KRYLOV (1962). The trial-and-error procedure for finding the undetermined constants μ_1, μ_3 and C_1 can be simplified minimizing a function F given by

$$F = |\mu_1 - \mu_{1c}| + |\mu_3 - \mu_{3c}| + |1 - \mu_{2c}| + |1 - \mu_{5c}| \tag{40}$$

where μ_1 and μ_3 are assumed values, μ_{1c}, μ_{2c}, μ_{3c} and μ_{5c} are the computed values of moments μ given by (25). The results of numerical calculations obtained using the IBM 360/75 computer at the California Institute of Technology are given in Tables I and II. The constant C_2 appearing in the approximate solution for the upper end of the spectrum (equation (38)) can be evaluated after the numerical solution for the whole spectrum is obtained. The values of the constant C_2 for various K are given in Table III.

TABLE III.

Estimated values of C_2 by fitting equation (38) to the numerical solution of the whole spectrum.

K	0.01	0.1	0.5	1.0
C_2	1.0547	1.0669	1.0937	1.3730

The self-preserving spectra $\psi = \psi(\eta)$ for different values of K are given in Figure 1.

The curve for K = 0 corresponding to the case treated by FRIEDLANDER and WANG (1966) is given for comparison. The curve for K = 0.01 is not given since this curve lies very close to the curve for K = 0.

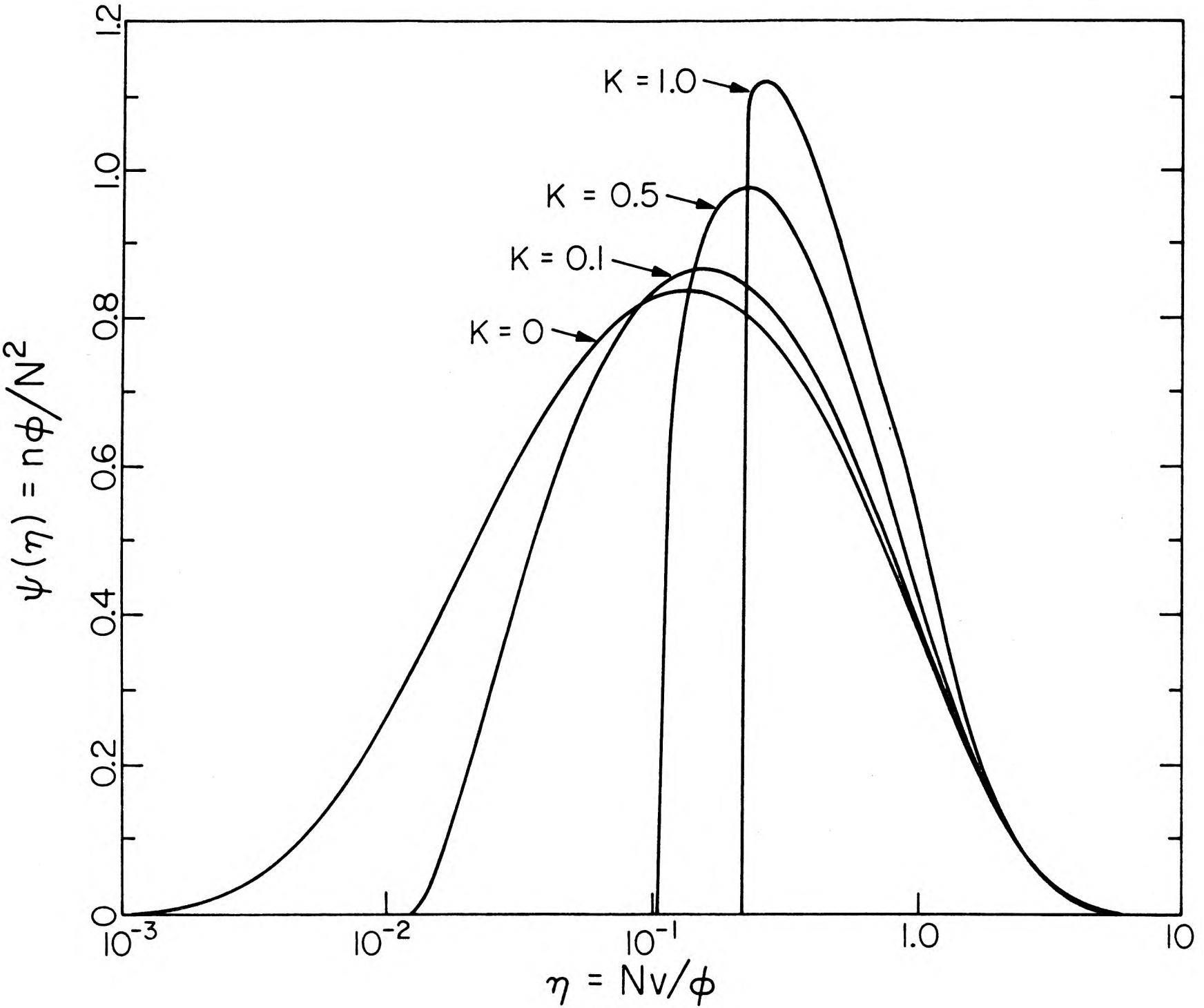

Fig. 1 SELF-PRESERVING PARTICLE SIZE DISTRIBUTION FOR SMOLUCHOWSKI COAGULATION WITH SIMULTANEOUS MAXWELLIAN CONDENSATION

TABLE I.

Self-preserving particle size distribution for Smoluchowski coagulation with simultaneous Maxwellian condensation obtained from equation (34) by a finite-difference method.

	η	$\psi(\eta)$		η	$\psi(\eta)$
K = 0.01	0.0010	0.0002	K = 0.5	0.1144	0.6422
	0.0020	0.0067		0.1544	0.9106
	0.0030	0.0244		0.2084	0.9752
	0.0041	0.0517		0.3109	0.9402
	0.0061	0.1133		0.3798	0.8885
	0.0100	0.2335		0.5126	0.7663
	0.0201	0.4567		0.6261	0.6624
	0.0301	0.5871		0.8452	0.5105
	0.0605	0.7682		1.2609	0.3136
	0.1103	0.8435		1.7020	0.1913
	0.2009	0.8306		2.0789	0.1224
	0.6036	0.5779		3.1013	0.0347
	1.0999	0.3497		4.1863	0.0095
	2.0041	0.1384		5.1131	0.0031
	6.6537	0.0006		6.2452	0.0008
K = 0.1	0.0133	0.0133	K = 1.0	0.2351	1.1178
	0.0243	0.2877		0.2872	1.1011
	0.0400	0.5487		0.3877	1.0143
	0.0540	0.6749		0.4735	0.9483
	0.0806	0.7945		0.5783	0.8183
	0.1088	0.8460		0.7064	0.7259
	0.1623	0.8659		0.8628	0.5806
	0.2958	0.8005		1.0538	0.4693
	0.4412	0.6991		1.2871	0.3252
	0.6582	0.5602		1.5721	0.2205
	1.0852	0.3575		1.9201	0.1379
	1.7892	0.1694		2.3452	0.0776
	3.2602	0.0356		3.1657	0.0268
	5.3752	0.0036		3.8666	0.0085
	7.2558	0.0004		4.7227	0.0017

TABLE II.

Values of moments μ_i (i = 1, 2, 3, 5), η_1, values of C_1 and the accuracy of calculations

K	μ_1		μ_2	μ_3		μ_5	η_1	C_1
	Assumed	Computed	Assumed 1.0 (required value) Computed	Assumed	Computed	Assumed 1.0 (required value) Computed		
0.01	1.2449	1.2464	0.9954	0.9048	0.9061	1.0050	0.0004	0.5403
0.1	1.2433	1.2291	0.9932	0.9057	0.9055	0.9935	0.0121	0.5466
0.5	1.2354	1.2368	0.9935	0.9073	0.9179	0.9835	0.1035	0.6085
1.0	1.1119	1.1191	0.9827	0.9353	0.9378	0.9969	0.2128	0.6927

VI. DISCUSSIONS

A. Limits of the Theory

According to equation (35) the behavior of $\psi(\eta)$ at $\eta = \eta_1$ depends on the value of $\varepsilon - \omega$. Three cases can be distinguished depending on whether $\varepsilon - \omega$ for which $\psi(\eta_1) = 0$, $\varepsilon - \omega = 0$ for which $\psi(\eta_1)$ is finite and $\varepsilon - \omega < 0$ for which $\psi(\eta_1)$ is infinite. Hence $\varepsilon - \omega = 0$ represents a critical case. Using the equations for ε and ω given by (35) this relationship can be expressed as a quartic equation in C:

$$a_4 C^4 + a_3 C^3 + a_2 C^2 + a_1 C - a_0 = 0 \tag{41}$$

where the coefficients a_i (i = 0, 1, 2, 3, 4) are given by

$$a_0 = \mu_3^2 + \mu_1^2 \mu_3^4 + 2\mu_1 \mu_3^3$$

$$a_1 = \frac{1}{9} - 2\mu_3^3 - 3\mu_1 \mu_3 - \frac{1}{3}\mu_1^2 \mu_3^2 + \frac{25}{9}\mu_1^3 \mu_3^3 - 2\mu_1 \mu_3^4$$

$$a_2 = -\frac{1}{3}\mu_3 - \mu_3^4 - \mu_1^2 - \frac{4}{3}\mu_1 \mu_3^2 + 5\mu_1^3 \mu_3^3$$

$$a_3 = \frac{8}{3}\mu_1 \mu_3^3$$

$$a_4 = \frac{4}{9}\mu_3^3$$

To each value of C there corresponds a solution $\psi = \psi(\eta)$ with particular values for the moments μ_1 and μ_3 so that μ_1 and μ_3 are both functions of C. The functional dependence, however, must be evaluated numerically. An estimate of the critical C can be made in the following way: The numerical solutions show that with increasing values of C the curves become narrower which means that condensation

tends to narrow the size spectrum. As shown above the deviations of moments μ_1 and μ_3 from unity serve as an index of the polydispersity of the system. Consequently, it can be expected that μ_1 is a decreasing function of C while μ_3 is an increasing function of C both approaching unity.

One extreme case is $\mu_1 = \mu_3 = 1$. Equation (41) in this case becomes

$$C^4 + 6C^3 + 3C^2 - 10C - 9 = 0 \qquad (42)$$

According to Descartes' rule this equation has no more than one positive root. Since for C = 1 the left side of (42) is negative and for C = 2 positive, This unique positive root lies between 1 and 2.

The second extreme case is Smoluchowski coagulation without condensation for which $\mu_1 = 1.248 \approx 1.25$ and $\mu_3 = 0.9046 \approx 0.9$.
Equation (41) becomes

$$0.32C^4 + 2.43C^3 + 3.23C^2 - 2.87C - 3.66 = 0 \qquad (43)$$

Again Descartes' rule requires that the positive root of (43) which also lies between 1 and 2 is the only positive root of this equation. Thus it appears that the critical value of C lies between positive roots of (42) and (43) i.e., between 1 and 2 so the theory is limited to values of C smaller than the order of unity.

B. Role of Homogeneous Nucleation

To estimate the order of magnitude of C for typical conditions, the parameter B appearing in (12) and defined by (9) must be known. Typical values for the constants appearing in B for water vapor are (FUCHS, 1959 ; WEAST, 1965):

$\rho \approx 1\ g\,cm^{-3}$, $L \approx 2.34 \times 10^{11}\ erg\ g^{-1}$, $M = 18\ g\ mol^{-1}$,

$\kappa = 2.5 \times 10^{5}\ erg\ sec^{-1}\ cm^{-1}\ grad^{-1}$, $R = 8.31 \times 10^{7}\ erg\ mol^{-1}\ grad^{-1}$

$D \approx 0.25\ cm^{2}\ sec^{-1}$, $P_s \approx 24 \times 10^{3}\ dyn\ cm^{-2}$,

so that we get $B \approx 10^{-5}\ cm^{2}\ sec^{-1}$.

Since the theory is limited to small values of C from (12) it follows that S must be very close to unity. Much higher values of the saturation ratio are required for homogeneous nucleation than for vapor condensation on foreign particles (MASON, 1957). Thus neglecting new particle formation by homogeneous nucleation is justified for the theory discussed in this paper.

C. Relationship Between Surface Area and Saturation Ratio

The moment μ_4 is defined by (21) or by (28) and by (30) $0 < \mu_4 < 1$. This moment can be expected to increase with increasing C. The value of μ_4 has been calculated numerically for K = 1 and found to be $\mu_4 = 0.9505$. Substitution of this value into (20) gives for K = 1

$$\sigma = \sigma_0 = 4.5964\ \phi^{\frac{2}{3}} N^{\frac{1}{3}} = \text{CONSTANT} \tag{44}$$

According to (12) and (20) the surface concentration σ is proportional to the saturation ratio S. Using the values of moments μ_1 and μ_3 for K = 1 given in Table II we get C = 1.09. Thus, for K = 1 the values of μ_4 and C are known so that the proportionality coefficient between σ and S can be calculated for particular values of μ, T and B.

Appendix I. Derivation of Equation (4) from Equation (1)

Integrating Equation (1) with respect to v from 0 to ∞ gives

$$\int_0^\infty \left\{ \frac{\partial n}{\partial t} + \frac{\partial}{\partial v}(I \cdot n) \right\} dv = \frac{1}{2}\int_0^\infty \int_0^v \beta(\hat{v}, v-\hat{v})\, n(\hat{v},t)\, n(v-\hat{v},t)\, d\hat{v}\, dv + \int_0^\infty \int_0^\infty \beta(v,\hat{v})\, n(\hat{v},t)\, n(v,t)\, d\hat{v}\, dv$$

Let

$$A = \int_0^\infty \left\{ \frac{\partial n}{\partial t} + \frac{\partial}{\partial v}(I \cdot n) \right\} dv$$

$$B = \frac{1}{2}\int_0^\infty \int_0^v \beta(\hat{v}, v-\hat{v})\, n(\hat{v},t)\, n(v-\hat{v},t)\, d\hat{v}\, dv$$

$$C = \int_0^\infty \int_0^\infty \beta(v,\hat{v})\, n(\hat{v},t)\, n(v,t)\, d\hat{v}\, dv$$

Then $A = \frac{\partial}{\partial t}\int_0^\infty n(v,t)\, dv + \int_0^\infty \frac{\partial}{\partial v}(I \cdot n)\, dv$ and since $N(t) = \int_0^\infty n(v,t)\, dv$ we have

$$A = \frac{dN(t)}{dt} + \int_0^\infty \frac{\partial}{\partial v}(I \cdot n)\, dv$$

The second term of the above expression represents the rate of change of the total number concentration due to condensation. Since the assumption is made that condensation does not change the total number concentration (homogeneous nucleation is not taken into account) this term must be zero.

Thus, $A = \frac{dN(t)}{dt}$

Let $$y = \frac{\tilde{v}}{v - \tilde{v}}$$

Then

$$\tilde{v} = 0 \qquad \text{at} \qquad y = 0$$

$$\tilde{v} = v \qquad \text{at} \qquad y = \infty$$

$$B = \frac{1}{2}\int_0^\infty\int_0^\infty \beta\left(\frac{y}{1+y}v, \frac{1}{1+y}v\right) n\left(\frac{y}{1+y}v, t\right) n\left(\frac{v}{1+y}, t\right)\frac{v}{(1+y)^2}\,dy\,dv$$

$$= \frac{1}{2}\int_0^\infty\int_0^\infty \beta\left(\frac{yv}{1+y}, \frac{v}{1+y}\right) n\left(\frac{yv}{1+y}, t\right) n\left(\frac{v}{1+y}, t\right)\frac{v}{(1+y)^2}\,dv\,dy$$

Let $$\xi = \frac{yv}{1+y}$$

Then $$v = 0 \qquad \text{at} \qquad \xi = 0$$

$$v = \infty \qquad \text{at} \qquad \xi = \infty$$

So $$B = \frac{1}{2}\int_0^\infty\int_0^\infty \beta\left(\xi, \frac{\xi}{y}\right) n(\xi, t)\, n\left(\frac{\xi}{y}, t\right)\frac{\xi}{y^2}\,d\xi\,dy$$

$$= \frac{1}{2}\int_0^\infty\int_0^\infty \beta\left(\xi, \frac{\xi}{y}\right) n(\xi, t)\, n\left(\frac{\xi}{y}, t\right)\frac{\xi}{y^2}\,dy\,d\xi$$

Furthermore, let $$\eta = \frac{\xi}{y}$$

then $$y = 0 \qquad \text{at} \qquad \eta = \infty$$

$$y = \infty \qquad \text{at} \qquad \eta = 0$$

Hence

$$B = -\frac{1}{2}\int_0^\infty\int_\infty^0 \beta(\xi, \eta)\, n(\xi, t)\, n(\eta, t)\,d\eta\,d\xi = \frac{1}{2}\int_0^\infty\int_0^\infty \beta(v, \tilde{v})\, n(v, t)\, n(\tilde{v}, t)\,d\tilde{v}\,dv$$

$$\therefore\ A = -\frac{1}{2}\int_0^\infty\int_0^\infty \beta(v, \tilde{v})\, n(v, t)\, n(\tilde{v}, t)\,d\tilde{v}\,dv$$

Appendix II. Derivation of Eqn. (7) from Eqn. (1)

Multiplying Eqn. (1) by v and integrating with respect to v from o to ∞ gives

$$\int_0^\infty \left\{ v \frac{\partial n}{\partial t} + v \frac{\partial}{\partial v}(I \cdot n) \right\} dv = \frac{1}{2} \int_0^\infty \int_0^v v \beta(\hat{v}, v-\hat{v})\, n(\hat{v}, t)\, n(v-\hat{v}, t)\, d\hat{v}\, dv - \int_0^\infty \int_0^\infty v \beta(v, \hat{v})\, n(v, t)\, n(\hat{v}, t)\, d\hat{v}\, dv$$

Let $A = \int_0^\infty \left\{ v \frac{\partial n}{\partial t} + v \frac{\partial}{\partial v}(I \cdot n) \right\} dv$

$$B = \frac{1}{2} \int_0^\infty \int_0^v v \beta(\hat{v}, v-\hat{v})\, n(\hat{v}, t)\, n(v-\hat{v}, t)\, d\hat{v}\, dv$$

$$C = \int_0^\infty \int_0^\infty v \beta(v, \hat{v})\, n(v, t)\, n(\hat{v}, t)\, d\hat{v}\, dv$$

In B, let $y = \dfrac{\hat{v}}{v - \hat{v}}$

then $B = \frac{1}{2} \int_0^\infty \int_0^\infty \beta\left(\frac{yv}{1+y}, \frac{v}{1+y}\right) n\left(\frac{yv}{1+y}, t\right) n\left(\frac{v}{1+y}, t\right) \frac{v^2}{(1+y)^2}\, dv\, dy$

Let $\xi = \frac{yv}{1+y}$

then $B = \frac{1}{2} \int_0^\infty \int_0^\infty \beta\left(\xi, \frac{\xi}{y}\right) n(\xi, t)\, n\left(\frac{\xi}{y}, t\right) \frac{(1+y)\xi^2}{y^3}\, dy\, d\xi$

Let $\eta = \frac{\xi}{y}$

$$B = \frac{1}{2} \int_0^\infty \int_0^\infty \beta(\xi, \eta)\, n(\xi, t)\, n(\eta, t)(\eta + \xi)\, dy\, d\xi$$

$$= \frac{1}{2} \int_0^\infty \int_0^\infty \beta(v, \hat{v})\, n(v, t)\, n(\hat{v}, t)(v + \hat{v})\, dv\, d\hat{v} = C$$

Therefore, $A = O$ (1)

Next consider

$$\frac{\partial}{\partial t}(nv) = n \frac{\partial v}{\partial t} + v \frac{\partial n}{\partial t} \qquad (2)$$

Since v is a function of time t only, the partial differentiation with respect to t is equal to total differentiation.

Thus $\frac{\partial v}{\partial t} = \frac{dv}{dt}$

and further by definition of rate of condensation

$$I = \frac{dv}{dt}$$

therefore, Eqn. (2) becomes

$$\frac{\partial}{\partial t}(vn) = nI + v\frac{\partial n}{\partial t}$$

or $$v\frac{\partial n}{\partial t} = \frac{\partial}{\partial t}(vn) - nI$$

hence $$A = \int_0^\infty \left\{\frac{\partial}{\partial t}(vn) - nI + v\frac{\partial}{\partial v}(In)\right\} dv \qquad (3)$$

$$\int_0^\infty \frac{\partial}{\partial t}(vn)\,dv = \frac{\partial}{\partial t}\int_0^\infty v\,n\,dv$$

By definition, $\int_0^\infty v\,n\,dv = \phi(t)$ is a function of t only.

Therefore $$\int_0^\infty \frac{\partial}{\partial t}(vn)\,dv = \frac{d\phi(t)}{dt} \qquad (4)$$

In the Appendix I we have shown that $\int_0^\infty \frac{\partial}{\partial v}(In)\,dv$, which represents the rate of change of the total number concentration, is zero. So the term $\int_0^\infty v\frac{\partial}{\partial v}(In)\,dv$ represents the average rate of the change of the total number concentration. Since we assume that condensation does not change the total number concentration. The average rate is, of course, zero.

Thus, $$\int_0^\infty v\frac{\partial}{\partial v}(In)\,dv = 0 \qquad (5)$$

From Eqns. (3), (4) & (5) we have

$$A = \frac{d\phi}{dt} - \int_0^\infty \eta I \, d\upsilon$$

and by (1) $A = 0$, therefore

$$\frac{d\phi}{dt} = \int_0^\infty \eta I \, d\upsilon$$

Appendix III. Derivation of the Maxwell Equation for the Rate of Condensation: Equation (9)

The theory of vapor condensation on particles in a gaseous medium was first investigated by Maxwell. Maxwell assumed that the vapor concentration at the surface of the particle was equal to its equilibrium density, Co. This assumption is true when the Knudsen number is very small, i.e., the particle radius r is much greater than the vapor molecule mean free path.

In the case of stationary condensation, the rate I_m of diffusion of the vapor of the particle across any spherical surface with radius ρ may be written as

$$I_m = -4\pi\rho^2 D \frac{dC}{d\rho} \tag{1}$$

where D the diffusivity of the vapor, C its concentration.

The boundary conditions are

(i) $C = C_\infty$ at $\rho = \infty$ (2)

(ii) $C = C_0$ at $\rho = r$ (Knudsen number is small)

The solution of (1) and (2) gives

$$I_m = 4\pi r D (C_0 - C_\infty) \tag{3}$$

If the vapor obeys the ideal gas law, then

$$C = \frac{pM}{RT} \tag{4}$$

where p is partial vapor pressure, M molecular weight, R gas constant, and T absolute temperature. Eqn. (3) becomes

$$I_m = \frac{4\pi r D M}{R\bar{T}} (p_0 - p_\infty) \tag{5}$$

where $\overline{T}$ is mean value of the absolute temperature between T_o and $T\infty$. Next, consider the temperature drop caused by condensation. If the heat transfer by convection and radiation are negligible and the conductivity of the gaseous medium is constant, then

$$I_H = -4\pi\rho^2 \kappa \frac{dT}{d\rho} \tag{6}$$

where κ is thermal conductivity of the gaseous medium. The boundary conditions are

(i) $T = T\infty$ (temperature of the medium) at $\rho = \infty$

(ii) $T = T_o$ (temperature of the surface of particle) at $\rho = r$ (7)

The solution of (6) and (7) gives

$$T_o - T\infty = \frac{r}{\rho} (T_o - T\infty) \tag{8}$$

The heat flux to the drop from the surrounding space due to conductivity of the medium is

$$I_H = 4\pi r \kappa (T\infty - T_o) \tag{9}$$

In stationary condensation, the quantity of heat transferred to particle equals the amount released in condensation, i.e.,

$$I_H = -I_m \cdot L \tag{10}$$

Where L is the latent heat of condensation of the liquid, the minus sign is used because of condensation.

Eqn. (5) is substituting into Eqn. (10) gives

$$T_o - T\infty = \frac{LDM}{\kappa R \overline{T}} (P_o - P_\infty) \tag{11}$$

Hence, Eqn. (5) becomes

$$I_m = -\frac{4\pi r \kappa}{L} (T\infty - T_o) \tag{12}$$

In the case of condensation, the Clapeyron-Clausisus equation

$$\frac{dp}{dT} = \frac{\lambda}{T \Delta \bar{v}} \tag{13}$$

may be written as

$$\frac{dp}{dT} = \frac{L}{T_0 (C_g - C_l)} \tag{14}$$

If we neglect the volume of the liquid compared to that of the vapor, then with the assumption of the ideal gas for the vapor,

$$\frac{dp}{dT_0} = \frac{p L M}{T_0^2 R} \tag{15}$$

Let p_s be the pressure of the saturated vapor at $T\infty$, then

$$\int_{p_s}^{p_0} \frac{dp}{p} = \int_{T_0}^{T\infty} \frac{L M dT}{R T^2} \tag{16}$$

$$\ln \frac{p_0}{p_s} = -\frac{ML}{R}\left(\frac{1}{T_0} - \frac{1}{T_\infty}\right) \tag{17}$$

If $T_0 - T\infty$ is small, then

$$\frac{p_0}{p_s} \approx \exp\left[-\frac{LM}{R}\frac{T_\infty - T_0}{T_\infty^2}\right] = \exp\left[\frac{L^2 M \cdot I_m}{4\pi r \kappa R T_\infty^2}\right] \tag{18}$$

From Eqn. (11)

$$\frac{p_0 - p_\infty}{p_s} = \frac{\kappa \bar{T}(T_0 - T_\infty)}{L D M p_s} = -\frac{\bar{T} R I_m}{D M p_s \cdot 4\pi r} \approx -\frac{I_m R T_\infty}{4\pi r D M p_s} \tag{19}$$

Let $S = \frac{p_\infty}{p_s}$

then $S = \frac{p_0}{p_s} + \frac{I_m L T_\infty}{4\pi r D M p_s}$

$$= \exp\left[\frac{L^2 M I_m}{4\pi r \kappa R T_\infty^2}\right] + \frac{I_m R T_\infty}{4\pi r D M p_s}$$

$$\approx 1 + \frac{I_m}{4\pi r}\left(\frac{L^2 M}{\kappa R T_\infty^2} + \frac{R T_\infty}{D M p_s}\right)$$

$$\therefore \quad v = \frac{4}{3}\pi r^3$$

$$r = \left(\frac{3v}{4\pi}\right)^{\frac{1}{3}}$$

$$\therefore \quad 4\pi r = (4\pi)^{\frac{2}{3}} 3^{\frac{1}{3}} v^{\frac{1}{3}}$$

If I_m is in volume per unit time, we must divide I_m by density of the liquid. Hence, let

$$B = \frac{3^{\frac{1}{3}}(4\pi)^{\frac{2}{3}}}{\frac{\rho L^2 M}{K R T^2} + \frac{\rho R T}{D M P_s}}$$

we get $I_m = B(S-1) v^{\frac{1}{3}}$

Appendix IV. Numerical Solution of the General Ordinary and Nonlinear Integro-Differential Equation:

$$\int_0^{\eta} f_1(\eta,\hat{\eta})\,\psi(\hat{\eta})\,\psi(\eta-\hat{\eta})\,d\hat{\eta} + f_2(\eta,\mu_1,\cdots,\mu_n)\frac{d\psi}{d\eta} + f_3(\eta,\mu_1,\cdots,\mu_n)\psi = 0 \tag{1}$$

with constraints:

(i) $$\int_0^{\infty} \psi(\eta)\,d\eta = 1$$

(ii) $$\int_0^{\infty} \eta\,\psi(\eta)\,d\eta = 1$$

(iii) $$\int_0^{\infty} \eta^{\alpha(i)}\psi(\eta)\,d\eta = \mu_i \qquad i = 1,\cdots,n$$

where $\alpha(i)$ is a function depends on i.

It seems very unlikely to find the analytic solution of the above quation which appears frequently in the theory of aerosols. The present study attempts to solve this equation numerically. As an example, this equation will be solved for the case of Maxwellian condensation and Smolchowski coagulation.

To facilitate the numerical calculation, the following transformation is introduced (WANG and FRIEDLANDER, 1966).

$$\eta = e^x \tag{2}$$

$$\psi(\eta) = Y(x) \tag{3}$$

The advantage of the above transformation is that the function Y(x) looks like a normal distribution. The argument x ranges from $-\infty$ to $+\infty$. Using this transformation, Eqn. (1) becomes

$$\int_{-\infty}^{x} f_1(e^x, e^{\hat{x}})\,Y(\hat{x})\,Y(\ln(e^x - e^{\hat{x}}))\,e^{\hat{x}}\,d\hat{x} + e^x f_2(e^x,\mu_1,\cdots,\mu_n)\frac{dY}{dx} + f_3(e^x,\mu_1,\cdots,\mu_n)\,Y(x) = 0 \tag{4}$$

Furthermore, let $$z = \frac{2}{3}(x - \tilde{x}) \tag{5}$$

The integral term then becomes

$$G_T(x) = \frac{3}{2}\int_0^\infty f_1(e^x,\ e^{x-\frac{3}{2}z})\,Y(x-\tfrac{3}{2}z)\,Y(x+\ln(1-e^{-\frac{3}{2}z}))\,e^{x-\frac{3}{2}z}\,dz$$

$$= \frac{3}{2}e^x\int_0^\infty [\,e^{-\frac{3}{2}z} f_1(e^x, e^{x-\frac{3}{2}z})\,Y(x-\tfrac{3}{2}z)\,Y(x+\ln(1-e^{-\frac{3}{2}z}))\,e^{-z}\,dz \tag{6}$$

The advantage of the transformation (5) is that the integral term can be transformed into the following form:

$$\int_0^\infty F(z)\,e^{-z}dz \tag{7}$$

The above integral can be interagated by the 32-point Gaussian-Laguerre quadrature formula which is a very general quadrature, and the subroutine is available in all computing facilities.

After these two transformations, Eqn. (1) becomes

$$G_T(x) + e^{-x} f_2(e^x, \mu_1, \cdots, \mu_n)\frac{dY}{dx} + f_3(e^x, \mu_1, \cdots, \mu_n)\,Y(x) = 0 \tag{8}$$

or $$\frac{dY(x)}{dx} = H(x, Y) \tag{9}$$

where $$H(x, Y) = -\frac{G_T(x) + f_3(e^x, \mu_1, \cdots, \mu_n)}{e^{-x} f_2(e^x, \mu_1, \cdots, \mu_n)} \tag{10}$$

Equation (9) is a first order ordinary differential equation. Among the approximate methods which exist at present, the finite difference methods are probably the most accurate. The Adams extrapolation method will be used.

The finite difference methods are based on the integral form of Eqn. (9), which is

$$Y(x_{i+1}) = Y(x_i) + \int_{x_i}^{x_{i+1}} H(x, Y(x))\,dx \tag{11}$$

In the Adams extrapolation method, the function $H(x, Y)$ under the integral sign in Eqn. (11) is replaced by the interpolation polynomial $P(x)$ which takes the values $f_{i-p}, \cdots, f_{i-1}$ at the point $x_{i-p}, \cdots, x_{i-1}$ respectively. In effect, we evaluate the integral by means of the quadrature formula

$$Y_{i+1} = Y_i + h\left(H_i + \frac{1}{2}\nabla H_i + \frac{5}{12}\nabla^2 H_i + \frac{3}{8}\nabla^3 H_i + \frac{251}{720}\nabla^4 H_i + \cdots\right) \qquad (12)$$

The truncation after $\nabla^4 H_i$ will be used in this solution of Eqn. (9), where

$$Y_i = Y(x_i)$$

$$H_i = H(x_i, Y_i)$$

$$\nabla^{(p)} H_i = \nabla(\nabla^{(p-1)} H_i) \qquad p \geq 2$$

$$\nabla^{(1)} H_i = \nabla H_i = H_i - H_{i-1}$$

In the finite difference method, it is always needed to have a sequence of approximations H_i before we can start the step-by-step procedures defined by Eqn. (12). Consequently, the finite difference methods have two distinct stages:

(i) Calculation of starting values which are obtained by some other means, for example, using the analytic solution of the Eqn. (1) for certain interval of η (for example, when η is small or η is large). This will bring another constant which is equivalent of addition of another constraint. We will discuss the constraints later.

(ii) Main calculation, step by step as far as required. Due to the undetermined constants $\mu_1, \cdots, \mu_n$ and the constraints (i) and

(ii) a trial-and-error procedure is necessary. The method assumes the undetermined constants μ_i's and then proceeds the numerical calculation. After the calculation is completed, the constraints (i)-(iii), are calculated. Let us denote them $U0$, $U1$ and μ_{ic}'s respectively, and then define the following function

$$F = |1 - U0| + |U1 - 1| + \sum_{i=1}^{n} |\mu_i - \mu_{ic}| \tag{13}$$

The problem now is to minimize the function F subject to the constraints (i)-(iii). An optimization program AMOEBA is written for obtaining μ_{ic}'s such that function F has a minimum.

As an example, Eqn. (34) is solved by the method described above. We have

$$f_1(\eta, \tilde{\eta}) = 1 + (\eta - \tilde{\eta})^{\frac{1}{3}} \tilde{\eta}^{-\frac{1}{3}} \tag{14}$$

$$f_2(\eta, \mu_1, \mu_3, c) = \eta + \mu_1 \mu_3 \eta + \mu_3 c \eta - c \eta^{\frac{1}{3}} \tag{15}$$

$$f_3(\eta, \mu_1, \mu_3, c) = 2\mu_1 \mu_3 - \mu_3 \eta^{-\frac{1}{3}} - \mu_1 \eta^{\frac{1}{3}} + \mu_3 c - \frac{1}{3} c \eta^{-\frac{2}{3}} \tag{16}$$

constraints $\alpha(i) = \frac{1}{3}(i-2)$

i.e., $$\int_0^\infty \eta^{\frac{1}{3}(i-2)} \psi(\eta) d\eta = \mu_i \qquad i = 1, 2, 3, 5 \tag{17}$$

where μ_2, μ_5 are constraints (i) and (ii) respectively. The result of the above calculation is given in TABLE I and II. The computer program written in FORTRAN IV is given in APPENDIX V.

Appendix V. Computer Program

A computer program of the solution of general nonlinear intego-differential equation with the example of solving Eqn. (34) is given. In using the computer program, the functions $f_1(\tau, \mu_1, \cdots, \mu_n)$, $f_2(\tau, \mu_1, \cdots, \mu_n)$, $f_3(\tau, \mu_1, \cdots, \mu_n)$ must be given in the SUBROUTINE QF. Two subroutines are also included. The first SUBROUTINE QF is mainly responsible for solving the integro-differential equation. The SUBROUTINE AMOEBA is a minimization program using the contraction method shrink the simplex toward a new minimum. If instead a maximum is found, then reflect the current maximum through centroid. Finally, test of convergence is given.

```
C
C*****NUMERICAL SOLUTION OF THE NONLINEAR INTEGRRO-DIFFERENTIAL EQUATION
C
C
C*****NUMERICAL SOLUTION OF THE TRANSFORMED KINETIC EQUATION :
C      SMOLUCHOWSKI COAGULATION AND MAXWELLIAN CONDENSATION
C
C*****CSTAR .NE. ZERO
C
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*4 QY,QP,QF,XETA(200),YY(200)
      DIMENSION QY(4),QP(2,6),CHECK(5),ETA(200),Y(200)
      EXTERNAL QF
      COMMON /PARM/ CHECK,BBC,BBW,ETA1,CSTAR,ETA,Y,RK,A,B,C1,NBC
101   FORMAT(9F8.0)
102   FORMAT(22X,'ETA',22X,'PSI')
103   FORMAT(1H1,48X,'A',24X,'B',23X,'C1',//)
104   FORMAT(12X,'GUESSED VALUE',3(10X,E15.8),//)
105   FORMAT(4(10X,E15.8))
106   FORMAT(9X,'CALCULATED VALUE',2(10X,E15.8),//)
107   FORMAT(' INTEGRATION OF PSI(ETA) OVER ETA FROM ZERO TO INFINITY =
     1',E15.8,///,' INTEGRATION OF ETA*PSI(ETA) OVER ETA FROM ZERO TO IN
     2FINITY = ',E15.8//)
108   FORMAT(8X,'CSTAR =',E15.8,8X,'ALPHA =',E15.8,9X,'BETA =',E15.8,9X,
     1'ETA1 =',E15.8//,11X,' K =',E15.8//,11X,' F =',E15.8,9X,' MU4 =',E
     215.8,//)
100   READ(5,101) RK,A,B,C1,(QY(I),I=1,2)
      IF(A.LT.0.9D0.OR.A.GT.1.D0.OR.B.LT.1.D0.OR.B.GT.1.3D0) GO TO 1000
      QP(1,1)=A
      QP(2,1)=B
      CALL AMOEBA(QP,QY,2,1.E-3,QF)
      J=4
      CALL QF(QP(1,J),XX)
      WRITE(6,105) XX,CHECK(4)
      WRITE(6,103)
      WRITE(6,104) (QP(I,4),I=1,2),C1
      WRITE(6,106) CHECK(3),CHECK(1)
      WRITE(6,108) CSTAR,BBC,BBW,ETA1,RK,XX,CHECK(4)
      WRITE(6,107) CHECK(2),CHECK(5)
      WRITE(6,102)
      DO 25 I=1,NBC
25    WRITE(6,105) ETA(I),Y(I)
      GO TO 100
1000  STOP
      END
```

```
      SUBROUTINE QF(VV,XX)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*4 XX,VV
      DIMENSION Z(32),Q(32),X(200),Y(200),ETA(200),F(200,5),ZZ(2),VV(3),
     1XI(200),XJ(200),CHECK(5),ZI(32),ZJ(32),ZK(32),YZ(2),YOP(5,32)
      COMMON /PARM/ CHECK,BBC,BBW,ETA1,CSTAR,ETA,Y,RK,A,B,C1,NBC
      DATA Z/.11175139809793770D3,.98829542868283970D2,.88735340417892400
     12,.80187446977913520D2,.72687628090662710D2,.65975377287930530D2,
     2.59892509162134018D2,.54333721333396907D2,.49224394987306390D2,
     3.44509207995754938D2,.40145719771539442D2,.36100494805751974D2,
     4.32346629153964737D2,.28862101816323475D2,.25628636022459200D2,
     5.22630889013196774D2,.19855860940336055D2,.17292454336715315D2,
     6.14931139755522557D2,.12763697986742725D2,.10783018632539720D2,
     7.89829409242125960D1,.73581267331862410D1,.59039585041742439D1,
     8.46164567697496740D1,.34922132730219945D1,.25283367064257949D1,
     9.17224087764464540D1,.10724487538178176D1,.57688462930188643D0,
     A.23452610951961854D0,.44489365833267018D-1/
      DATA Q/.45105361938989742D-47,.13386169421062563D-41,
     1.26715112192401370D-37,.11922487600982224D-33,
     2.19133754944542243D-30,.14185605454630369D-27,
     3.56612941303973594D-25,.13469825866373952D-22,
     4.20544296737880454D-20,.21197922901636186D-18,
     5.15421338333938234D-16,.81718234434207190D-15,
     6.32378016577292665D-13,.97993792887270940D-12,
     7.23058994918913610D-10,.42813829710409289D-9,
     8.63506022266258067D-8,.76045678791207810D-7,
     9.74164045786675520D-6,.59345416128686329D-5,
     A.39203419679879472D-4,.21486491880136419D-3,
     B.98080330164495510D-3,.37388162946115248D-2,
     C.11918214834838557D-1,.31760912509175070D-1,
     D.70578623865717442D-1,.12998378628607176D0,
     E.19590333597288104D0,.23521322966984801D0,
     F.21044310793881323D0,.10921834195238497D0/
      DATA E1,E2,E3,E5/0.33333333333333333,0.66666666666666667,
     A0.41666666666666667,0.34861111111111111/
      F1(EDA,EDAB)=1.D0+((EDA-EDAB)/EDAB)**E1
      F2(EDA,X1,X3,C)=EDA+X1*X3*EDA+X3*C*EDA-C*EDA**E1
      F3(EDA,X1,X3,C)=2.D0*X1*X3-X3/EDA**E1-X1*EDA**E1+X3*C-C*E1/EDA**E2
      A=VV(1)
      B=VV(2)
      IF(A.LT.0.9D0.OR.A.GT.1.D0.OR.B.LT.1.D0.OR.B.GT.1.3D0) GO TO 28
      DO 30 J=18,32
      ZI(J)=1.5D0*Z(J)
      ZJ(J)=DLOG(1.D0-DEXP(-ZI(J)))
30    CONTINUE
      DX=0.1D0
      IMAX=175
      GO TO 29
28    XX=1.E7
      GO TO 11
29    CSTAR=RK*(1.D0+A*B)/A*0.5D0
      W=1.D0+A*B+CSTAR*A
      CSTARW=CSTAR/W
      BMW=3.D0*B/W
```

```
      BBC=0.5D0-BMW*A-1.5D0*A*CSTARW
      AB=2.D0*A*B
      CSTARA=CSTAR*A
      CSTAR1=CSTAR*E1
      XO=1.5D0*DLOG(CSTARW)
      IF(XO.LT.-10.1D0) XO=-10.1D0
      CSTW=DSQRT(CSTARW)
      ETA1=CSTW**3
      BBW=1.5D0*(A/CSTW+B*CSTW)/W
      AA=BBC+BBW
      BB=BBC-BBW
      XMIN=XO+5*DX
      DO 10 I=1,IMAX
      X(I)=XO+I*DX
      ETA(I)=DEXP(X(I))
      XI(I)=DEXP(X(I)*E1)
      XJ(I)=DEXP(X(I)*E2)
10    CONTINUE
C
C*****CALCULATION OF STARTING VALUES
C
      DO 18 I=1,5
      Y(I)=C1*DEXP(BMW*XI(I)-E1*X(I))*(XI(I)-CSTW)**AA*(XI(I)+CSTW)**BB
18    F(I,1)=-(AB-A/XI(I)-B*XI(I)+CSTARA-CSTAR1/XJ(I))/
     1(W-CSTAR/XJ(I))*Y(I)
      DO 12 J=2,5
      DO 12 I=J,5
12    F(I,J)=F(I,J-1)-F(I-1,J-1)
      Y(6)=Y(5)+DX*(F(5,1)+0.5D0*F(5,2)+E3*F(5,3)+0.375D0*F(5,4)+
     1E5*F(5,5))
      DO 13 I=6,IMAX
      QQ=0.D0
      DO 14 J=18,32
      ZZ(1)=X(I)-ZI(J)
      ZZ(2)=X(I)+ZJ(J)
      DO 15 K=1,2
      IF(ZZ(K)-XMIN) 16,16,17
16    IF(ZZ(K).LT.XO) GO TO 26
      ZZXX=DEXP(E1*ZZ(K))
      YZ(K)=C1*DEXP(-ZZ(K)*E1+ZZXX*BMW)*(ZZXX-CSTW)**AA*(ZZXX+CSTW)**BB
      GO TO 15
26    YZ(K)=0.D0
      GO TO 15
17    IK=(ZZ(K)-XO)*10.D0
      DEL=ZZ(K)-X(IK)
      YZ(K)=Y(IK)+DEL*(F(IK,1)+0.5D0*F(IK,2)+E3*F(IK,3)+0.375D0*F(IK,4)
     1+E5*F(IK,5))
15    CONTINUE
      ETAB=DEXP(ZZ(1))
      ZK(J)=F1(ETA(I),ETAB)*DEXP(-Z(J)*0.5D0)
14    QQ=QQ+ZK(J)*YZ(1)*YZ(2)*Q(J)
      RR=F3(ETA(I),B,A,CSTAR)*Y(I)+1.5D0*ETA(I)*QQ
      SS=F2(ETA(I),B,A,CSTAR)/ETA(I)
      F(I,1)=-RR/SS
```

```
C
C*****ADAMS EXTRAPOLATION METHOD
C
      DO 19 J=2,5
19    F(I,J)=F(I,J-1)-F(I-1,J-1)
      Y(I+1)=Y(I)+DX*(F(I,1)+0.5D0*F(I,2)+E3*F(I,3)+0.375D0*F(I,4)+
     1E5*F(I,5))
      IF(Y(I+1).LT.0.D0) GO TO 20
13    CONTINUE
20    NBC=I
C
C*****CALCULATION OF UNDETERMINED CONSTANTS AND CONTRAINTS
C
      DO 21 I=1,5
      REALI=DFLOAT(I)
      SUM=0.D0
      DO 22 J=18,32
      YOP(I,J)=X(NBC)-3.D0*Z(J)/(REALI+1.D0)
      IF(YOP(I,J)-XMIN) 24,24,23
24    IF(YOP(I,J).LT.XO) GO TO 27
      ZZXX=DEXP(E1*YOP(I,J))
      YPP=C1*DEXP(-YOP(I,J)*E1+ZZXX*BMW)*(ZZXX-CSTW)**AA*(ZZXX+CSTW)**BB
      GO TO 22
27    YPP=0.D0
      GO TO 22
23    IK=(YOP(I,J)-XO)*10.D0
      DEL=YOP(I,J)-X(IK)
      YPP=Y(IK)+DEL*(F(IK,1)+0.5D0*F(IK,2)+E3*F(IK,3)+0.375D0*F(IK,4)+
     1E5*F(IK,5))
22    SUM=SUM+YPP*Q(J)
      CHECK(I)=3.D0*SUM*DEXP((REALI+1.D0)*X(NBC)/3.D0)/(REALI+1.D0)
21    CONTINUE
      XX=DABS(CHECK(3)-A)+DABS(CHECK(1)-B)+DABS(CHECK(2)-1.D0)
     1+DABS(CHECK(5)-1.D0)
      IF(XX.GT.1.E-2) GO TO 11
      WRITE(6,103)
      WRITE(6,104) A,B,C1
      WRITE(6,106) CHECK(3),CHECK(1)
      WRITE(6,108) CSTAR,BBC,BBW,ETA1
      WRITE(6,107) CHECK(2),CHECK(5)
      WRITE(6,105) XX,RK
      WRITE(6,102)
      DO 25 I=1,NBC
25    WRITE(6,105) ETA(I),Y(I)
102   FORMAT(22X,'ETA',22X,'PSI')
103   FORMAT(1H1,48X,'A',24X,'B',23X,'C1',//)
104   FORMAT(12X,'GUESSED VALUE',3(10X,E15.8),//)
105   FORMAT(4(10X,E15.8))
106   FORMAT(9X,'CALCULATED VALUE',2(10X,E15.8),//)
107   FORMAT(' INTEGRATION OF PSI(ETA) OVER ETA FROM ZERO TO INFINITY =
     1',E15.8,///,' INTEGRATION OF ETA*PSI(ETA) OVER ETA FROM ZERO TO IN
     2FINITY = ',E15.8//)
108   FORMAT(8X,'CSTAR =',E15.8,8X,'ALPHA =',E15.8,9X,'BETA =',E15.8,9X,
     1'ETA1 =',E15.8//)
11    RETURN
      END
```

```
      SUBROUTINE AMOEBA(P,Y,N,E,F)
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                                                                       C
C  UPON ENTRY THE FOLLOWING PARAMETERS MUST BE PASSED:                  C
C                                                                       C
C     N -- THE NUMBER OF VARIABLES FOR THE MINIMIZATION.                C
C     E -- ABSOLUTE DELTA FUNCTION VALUE FOR DETERMINING CONVERGENCE.   C
C     F -- THE NAME OF A SUBROUTINE WHICH WHEN CALLED BY CALL F(V,X)    C
C          WHERE V IS AN ARRAY OF N VALUES WILL RETURN WITH THE COR-    C
C          RESPONDING FUNCTION VALUE IN X.                              C
C     P -- AN ARRAY OF DIMENSION (N,N+4) WITH INITIAL VALUES FOR THE    C
C          VARIABLES X(I) IN P(I,1) FOR I=1(1)N.                        C
C     Y -- A VECTOR OF DIMENSION (N+2) CONTAINING N DISPLACEMENTS       C
C          DX(I) IN Y(I) FOR I=1(1)N.  THESE VALUES DX(I) WILL BE USED  C
C          TO CONSTRUCT THE INITIAL SIMPLEX IN THE ARRAY P:             C
C               P(I,J)=X(I)+DELTA(J-1,I)*DX(I) FOR I=1(1)N,J=1(1)N+1,   C
C          WHERE DELTA(I,J) IS THE KRONECKER DELTA FUNCTION.            C
C                                                                       C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      EXTERNAL F
      DIMENSION P(N,1),Y(1)
      DATA RFACT1,RFACT2/-1.0,2.0/
      DATA CFACT1,CFACT2/0.5,0.5/
      DATA EFACT1,EFACT2/2.0,-1.0/
 2000 FORMAT(10X,E12.5)
 2010 FORMAT(10X,'MAX,MIN',5X,2(E12.5,5X))
 2020 FORMAT(10X,'CENTROID',5X,E12.5)
 2030 FORMAT(10X,'REFLECTION',5X,E12.5)
 2040 FORMAT(10X,'EXPANSION',5X,E12.5)
 2050 FORMAT(10X,'CONTRACTION',5X,E12.5)
 2060 FORMAT(10X,'SHRINK',5X,E12.5)
CCC  INITIALIZE SUBROUTINE PARAMETERS.
      FLN=FLOAT(N)
      NS=N+1
      NC=N+2
      NR=N+3
      NT=N+4
CCC  CONSTRUCT INITIAL SIMPLEX.
  100 DO 101 J=1,N
      DO 102 I=1,N
      P(I,J+1)=P(I,1)
      IF(I.EQ.J) P(I,J+1)=P(I,J+1)+Y(I)
  102 CONTINUE
  101 CALL F(P(1,J),Y(J))
      CALL F(P(1,NS),Y(NS))
CCC  FIND CURRENT MAX AND MIN.
  200 NH=NS
      NL=NS
      YH=Y(NS)
      YL=Y(NS)
      DO 201 I=1,N
      IF(Y(I).LE.YH) GO TO 202
      YH=Y(I)
      NH=I
```

```
      GO TO 201
  202 IF(Y(I).GE.YL) GO TO 201
      YL=Y(I)
      NL=I
  201 CONTINUE
       WRITE(6,2010) YH,YL
CCC  COMPUTE CENTROID.
  300 DO 301 I=1,N
      X=0.0
      DO 302 J=1,NS
      IF(J.EQ.NH) GO TO 302
      X=X+P(I,J)
  302 CONTINUE
  301 P(I,NC)=X/FLN
      CALL F(P(1,NC),YC)
       WRITE(6,2020) YC
CCC  REFLECT CURRENT MAX THROUGH CENTROID.
  400 DO 401 I=1,N
  401 P(I,NR)=RFACT1*P(I,NH)+RFACT2*P(I,NC)
      CALL F(P(1,NR),YR)
       WRITE(6,2030) YR
      IF(YR.LT.YL) GO TO 500
      X=YL
      DO 402 I=1,NS
      IF(I.EQ.NH) GO TO 402
      IF(Y(I).GT.X) X=Y(I)
  402 CONTINUE
      IF(YR.GT.X) GO TO 600
      NEW=NR
      GO TO 800
CCC  EXPAND.
  500 DO 501 I=1,N
  501 P(I,NT)=EFACT1*P(I,NR)+EFACT2*P(I,NC)
      CALL F(P(1,NT),YT)
      NEW=NT
       WRITE(6,2040) YT
      IF(YT.GE.YL) NEW=NR
      GO TO 800
CCC  CONTRACT.
  600 NEW=NH
      IF(YR.GT.YH) GO TO 601
      NEW=NR
      YH=YR
  601 DO 602 I=1,N
  602 P(I,NT)=CFACT1*P(I,NEW)+CFACT2*P(I,NC)
      CALL F(P(1,NT),YT)
       WRITE(6,2050) YT
      IF(YT.GT.YH) GO TO 700
      NEW=NT
      GO TO 800
CCC  SHRINK SIMPLEX TOWARD CURRENT MIN.
  700 DO 701 J=1,NC
      IF(J.EQ.NL) GO TO 701
      DO 702 I=1,N
```

```
  702 P(I,J)=0.5*(P(I,J)+P(I,NL))
      CALL F(P(1,J),Y(J))
  701 CONTINUE
      YC=Y(NC)
       WRITE(6,2060) YC
      GO TO 802
CCC  TEST FOR CONVERGENCE.
  800 DO 801 I=1,N
  801 P(I,NH)=P(I,NEW)
      YH=YR
      IF(NEW.EQ.NT) YH=YT
      Y(NH)=YH
  802 ERR=0.0
      DO 803 I=1,NS
  803 ERR=ERR+(Y(I)-YC)**2
      ERR=SQRT(ERR/FLN)
      IF(ERR.LT.E) GO TO 1000
       CALL ELAPSE
       WRITE(6,2000) ERR
CCC  UPDATE CYCLE DATA.
  900 GO TO 200
CCC  END OF MINIMIZATION.
 1000 RETURN
      END
```

NOMENCLATURE

Roman Letters

A_o	=	collision paramer of a polydisperse system, defined by Eqn. (5)
a_i (i=0, 1, 2, 3, 4)	=	dimensionless constant given in Eqn. (41)
B	=	proportionality coefficient in the Maxmell condensation Eqn. (9)
C	=	dimensionless parameter defined in Eqn. (12)
C_1, C_i'	=	integration constants defined in Eqn. (35) and Eqn. (35a) respectively
C_2	=	Integration constant defined in Eqn. (38)
D	=	diffusivity of vapor
F	=	function defined in Eqn. (40)
$f_v(v)$	=	normalized volume distribution function
I	=	rate of condensation
K	=	dimensionless constant defined by Eqn. (17)
k	=	Boltzmann's constant
L	=	latent heat
M	=	molecular weight of vapor
N(t)	=	total number concentration of particle at time t
N_o	=	initial number concentration, equal N(o)
$n(v,t)$	=	particle volume distribution function
p_s	=	saturated vapor pressure
p_v	=	actual vapor pressure
R	=	gas constant
r	=	radius of the particle
r_1	=	arithmetic mean radius of particles
r_2	=	mean square radius of particles
r_3	=	cubic mean radius of particles
r_H	=	harmonic mean radius of particles
S	=	saturation ratio
T	=	absolute temperature of the medium
t	=	time
v, $\hat{v}$	=	particle volumes
v^+	=	mean particle volume
x	=	dimensionless variable
Y(x)	=	dimensionless transformed distribution function
z	=	transformed variable

Greek Letters

$\beta(v, \hat{v})$	= collision parameter for particles of volume v and $\hat{v}$
ε	= dimensionless parameter defined in Eqn. (35)
η	= dimensionless independent variable defined in Eqn. (10)
η_i	= dimensionless parameter defined in Eqn. (35)
κ	= thermal conductivity of the medium
μ	= vecosity of the medium
$\mu_i (i = 1,2,3,4,5)$	= moment of the distribution function defined in Eqn. (25)
$\mu_{ic} (i = 1,2,3,5)$	= computed values of μ_i's
ρ	= density of liquid
$\sigma(t)$	= total surface concentration of particles at time t
σ_o	= $\sigma(0)$ initial total surface concentration of particle
$\phi(t)$	= total volume concentration at time t
ϕ_o	= $\phi(0)$ initial total volume concentration
$\psi(\eta)$	= dimensionless distribution defined in Eqn. (10)
ω	= dimensionless parameter defined in Eqn. (35)

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MEMORANDUM

March 10,1970

TO : Dr. L. LEES

FROM : F.S. LAI

SUBJECT : CANDIDACY EXAMINATION

DATE : March 17,1970

TIME : 1:30 p.m.

PLACE: 221 Spalding